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Model compound approach to design process and select catalysts for in-situ bio-oil upgrading

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ABSTRACT

Upgrading of pyrolysis bio-oil from biomass suggests great environmental and economical advantages for the production of renewable and sustainable energy sources. However, there are considerable challenges in the development of techno-economically feasible processes and catalysts. One promising approach is in-situ vapor phase upgrading, which demonstrates numerous benefits.

Due to the highly complex nature of bio-oil, understanding the reaction pathways for each kind of compound conversion is highly desirable for catalyst and process screening. Therefore, the study of model compounds is the first step in simplifying the complexity of the problem.

This investigation presents a summary of invaluable model compound based approach research to develop the fundamental processes and catalysts knowledge required to design upgrading strategies of fast pyrolysis bio-oil to achieve a stable product. Key upgrading reactions for the various oxygenated compounds available in pyrolysis vapor, comprising aldol condensation, deoxygenation, alkylation and aromatization are explained. Model compound studies have also been crucial to understanding catalyst behavior for a certain process and identifying potential means to mitigate catalyst deactivation. The knowledge gained from the model compound studies can be correlated to actual pyrolysis bio-oil vapor upgrading.

Contents

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1. Introduction

The importance of renewable energy sources has quickly increased due to the high price of crude oil, high demand of energy resources and environmental concerns caused by the use of fossil fuels. Among various energy resources, biomass recently has attracted significant interest as a promising renewable energy resource [1–4].

The abundance of lignocellulosic biomass and its low price make this feedstock attractive enough. Lignocellulosic biomass can be converted to liquid fuels via the pyrolysis process. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen [2–5].

Fast pyrolysis is one of the most promising technologies for the utilization of renewable biomass resources and it has attracted extensive attention in recent years [5–8]. It is characterized by very high heating rates, moderate temperatures (450–600 °C) and rapid quenching of the pyrolysis products [9].

Bio-oil derived from the degradation of lignin, cellulose and hemicelluloses is a complex mixture of oxygenated compounds. A typical bio-oil can contain more than 400 different compounds [10] with broad molecular range from 18 to 5000 g/mol or more [11]. These oxygenated compounds caused most of the deficiencies of bio-oil, such as its low heating value, adaptation with petroleum fuels, corrosiveness and instability under prolonged storage and transportation conditions [10–13].

For the aim of bio-oil's quality improvement, various approaches have been utilized comprising pyrolysis under reactive atmosphere [14–16], reduced pressure distillation [17], pyrolytic lignin removal [18], pyrolysis vapor upgrading at low pressure [19], high pressure thermal treatment [20], hydro-treatment at high pressure [21], solvent addition [22] and conversion of bio-oil's acidic compounds to esters over acid catalysts [23] and to ketones over base catalysts [24]. Most research efforts however focused on the upgrading of bio-oil by reducing its oxygen content.

While bio-oil was used as a feedstock for in-situ catalytic upgrading, a significant formation of tar and char, which could cause catalyst deactivation and bio-oil yield reduction, was observed during the process [25,26]. These drawbacks can be subsided using an in-situ biomass pyrolysis vapor upgrading process.

The in-situ catalytic upgrading of pyrolysis vapors, over HZSM-5 and HY zeolites in a fixed bed reactor, was carried out by Park et al. [27]. They compared their experimental results with the data from the study of Vitolo et al. [28]. In the case of in-situ catalytic upgrading of biomass pyrolytic vapors, approx. 10 wt% more bio-oil was yielded compared with the use of bio-oil as a feedstock.

As discussed above, one of the most promising processes to achieve upgraded bio-oil is the in-situ catalytic upgrading of biomass pyrolysis vapors. Unlike biomass catalytic pyrolysis, in which catalyst and feedstock are mostly mixed together, in-situ vapor upgrading is performed while biomass and catalyst are separated during the pyrolysis/upgrading process [14]. Pyrolysis vapor upgrading is carried out before vapor condenses, at atmospheric pressure, when vapors are passed through catalyst(s) bed(s). Fig. 1 indicates this type of pyrolysis/upgrading process. Depending on the catalysts' characteristics, different products can be selectively produced while enhanced deoxygenation can yield bio-oil with improved physical and chemical properties. Research is being directed towards the design of selective catalysts for either increasing the production of specific high added value chemicals (e.g. phenols) or minimizing the formation of undesirable bio-oil components (e.g. acids, carbonyls).

Bio-oil contains various oxygenated components originated from different biomass components (cellulose, hemicellulose and lignin) [29,30]. From techno-economical and environmental points of view, the challenge for future bio-refineries will not only include the elimination of oxygen from above mentioned compounds, but also the retention of carbon in the product, with minimum hydrogen consumption [31]. Conventional hydrotreating (HDT) process for bio-oil upgrading could fulfill the requirement of oxygen removal even by high hydrogen

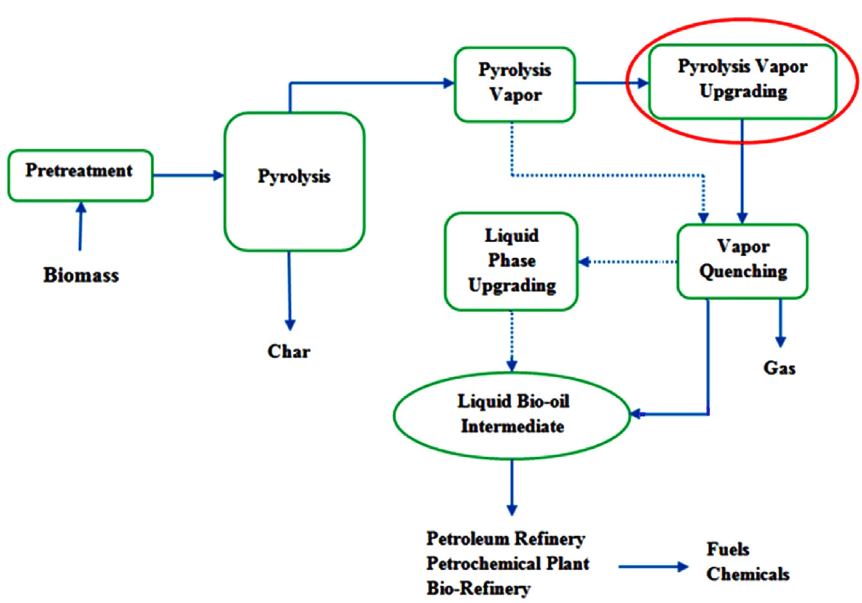


Fig. 1. Schematic of pyrolyis and upgrading process (highlighting pyrolysis vapor upgrading).

consumption, but it would fail to minimize carbon loss. HDT of the small oxygenates molecules would result in undesirable production of C_2–C_3 gases products rather than liquids in the target fuel range (C_6–C_{14}) [31].

As a result, it is important to evaluate these challenges and the role that different catalysts could play in the conversion of each of these families of oxygenates in the light of potential reaction paths. In his perspective, Hicks [32] emphasized that the development of highly selective and durable catalysts will be the key to the success of bio-fuel upgrading technologies. This contribution is focusing to review the research that have been done on bio-oil upgrading followed by deoxygenation with minimum hydrogen consumption and carbon loss. Within this context, model compound studies have been invaluable to identify catalysts and reaction conditions that are favorable for the desired reactions. Model compound studies have also been crucial to understanding catalyst behavior. The knowledge gained from the model compound studies can be applied to convert mixtures and actual pyrolysis oil vapors to gasoline range components. As an outcome of this survey, an integrated biofuel production facility with the process steps comprising lignocellulosic biomass pretreatment, pyrolyzing and vapors upgrading, using suggested catalysts, will be proposed.

In biomass to bio-fuel research following two important goals are considered: improvement of bio-fuel cost competitiveness and increase its potential so as to substitute petroleum. These two could be somehow achieved by minimizing carbon loss as well as hydrogen consumption. In addition, better control of the products selectivity can facilitate incorporation of the upgraded product in petroleum refineries or blending operations.

2. Lignocellulosic biomass structure and pretreatment

Three main building blocks of biomass are cellulose, hemicellulose, and lignin. Cellulose (a crystalline glucose polymer) and hemicellulose (a complex amorphous polymer) make up to 60–90 wt% of terrestrial biomass. Lignin (a large polyaromatic compound) is the other major component of biomass [33].

Cellulose polymer chain is constructed by cellobiose monomers linked by β-(1,4)-glycosidic bonds. Hydrogen and van der Waals bonds link long chain cellulose polymers and cause the cellulose to be packed into microfibrils. Hemicelluloses and lignin cover the microfibrils [34].

Hemicellulose has branches with short chains comprising different sugars. This is the main difference between cellulose and hemicelluloses. These monosaccharides include pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and uronic acids (e.g., 4-*o*-methylglucuronic, D-glucuronic, and D-galactouronic acids) [35].

Lignin, which is present in the primary cell wall, is structured as a complex cross linked phenolic polymers. It provides structural

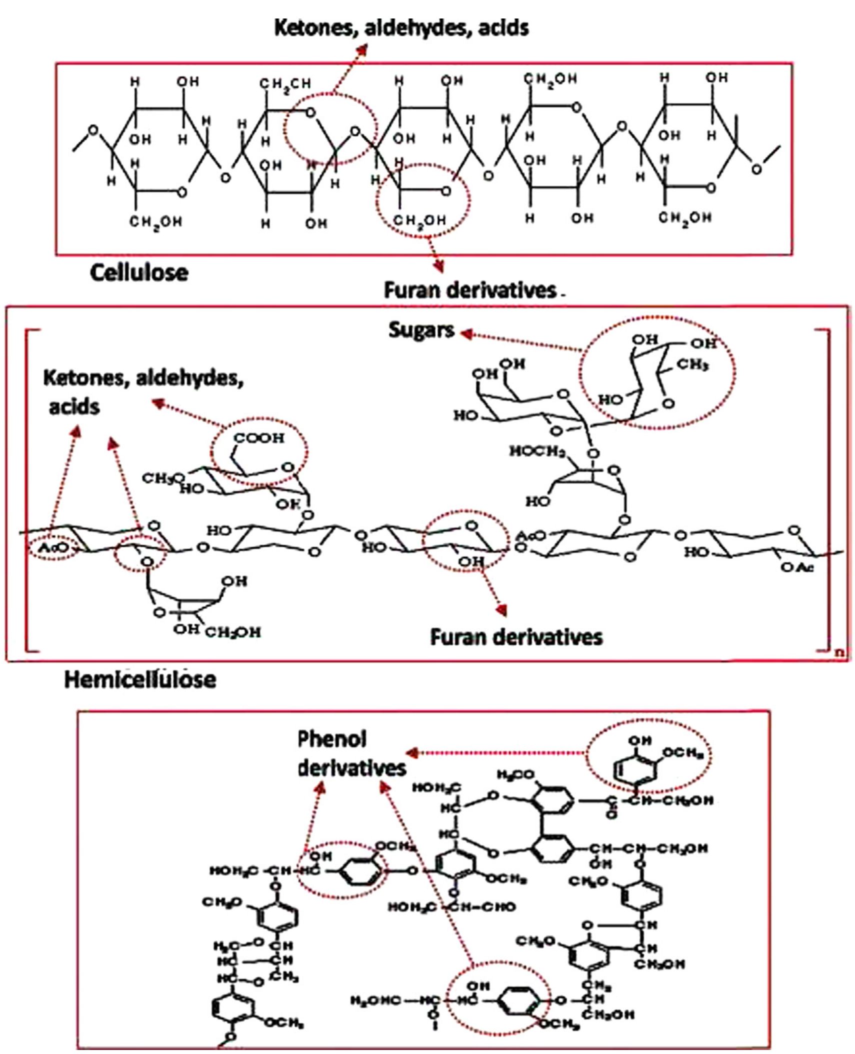


Fig. 2. The major chemical functionalities of bio-oil released during pyrolysis originated from cellulose, hemicellulose and lignin [38].

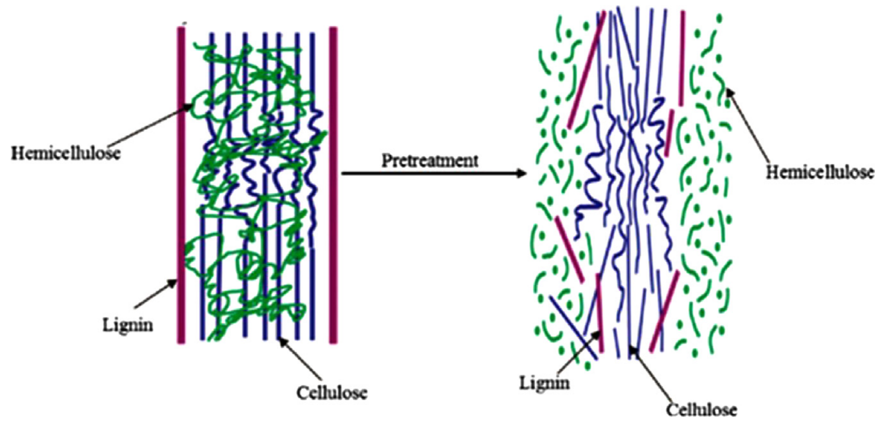


Fig. 3. Schematic of the role of pretreatment in the conversion of biomass to fuel [39].

support, impermeability, and resistance against microbial attack [36]. Three phenyl propionic alcohols exist as monomers of lignin: coniferyl alcohol, coumaryl alcohol and sinapyl alcohol. Alkyl–aryl, alkyl–alkyl, and aryl–aryl ether bonds link these phenolic monomers together. Lignin contents vary based on the type of biomass. Some, like herbaceous plants as grasses have lowest content of this complex phenolic compound, whereas softwoods have the highest content [37].

Fig. 2 [38] depicts the major components of lignocellulosic biomass and the probable pyrolysis products. As can be seen in Fig. 2, three main families of oxygenated compounds available in bio-oil can be defined as (1) acids, aldehydes, and ketones (such as acetic acid, acetol, acetone, etc.); (2) furfural, levoglucosan, and other sugar-derived compounds; and (3) lignin-derived phenolics [31].

In the conversion of lignocellulosic biomass to fuel, biomass needs to be passed through certain treatment. Pretreatment is an important tool for biomass-to-biofuels conversion processes. Fig. 3 shows the schematic of biomass pretreatment [39].

The beneficial effects of pretreatment of lignocellulosic materials have been recognized for a long time. The goal of pretreatment process is to break down lignin and hemicelluloses, reduce cellulose crystallinity and induce porosity to lingocellulosic materials [40]. Different pretreatment methods can be divided into physical (milling and grinding), physicochemical (steam pretreatment/autohydrolysis, hydrothermolysis, and wet oxidation), chemical (alkali, dilute acid, oxidizing agents, and organic solvents), biological, electrical, or a combination of these [39].

In some cases, combination of chipping, grinding, and/or milling can be applied to reduce cellulose crystallinity of lignocellulosic materials. The size of the materials is usually 10–30 mm after chipping and 0.2–2 mm after milling or grinding [41].

3. Biomass to bio-oil by fast pyrolysis

Fast pyrolysis is a promising process for biomass to bio-fuel conversion. The milled biomass feedstock is heated in the absence of air, forming a gaseous product and char. Four types of currently available commercial pyrolysis reactors are (1) fluidized beds, (2) circulating fluid beds, (3) ablative pyrolyzer, both cyclonic and plate type, and (4) vacuum pyrolyzer [33,42]. Fig. 4 [43] briefly shows the schematic of fast pyrolysis process.

Contrary to circulating fluid bed reactors, bubbling or fluid bed reactors have the merits of good temperature control, short residence time of vapors, efficient heat transfer and being technically feasible. Fluidizing gas flow rate controls the residence time which is higher for char than vapors. Short volatiles residence time is achieved by shallow bed depth and/or high fluidizing gas flow rate [33,42].

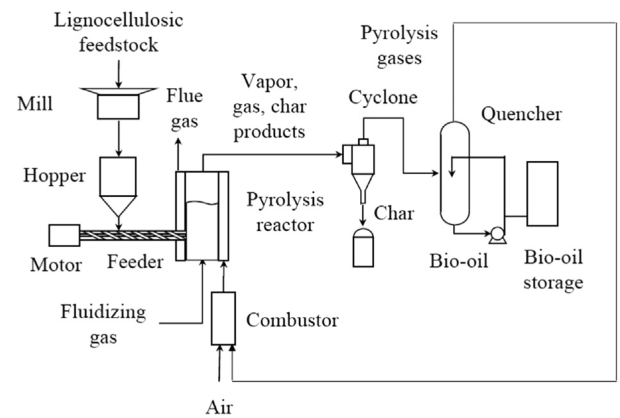


Fig. 4. Schematic of the Fast Pyrolysis System [43].

Small particle sizes of less than 2–3 mm are fluidized while the reactor is heated through hot walls, hot tubes, hot fluidization gas injection, and/or hot sand recycling. In contrast to circulating fluidized bed reactors, in this type of reactors, high quality bio-oil is produced due to low concentration of char. Contrary to fluid bed reactors, the char residence time in circulating fluid bed reactors is almost the same as the vapor and gas residence time [33,42].

In ablative pyrolyzer, biomass species are moved at high speed against a hot metal surface. Ablation of formed chars at a particle's surface maintains a high heat transfer rate. This can be achieved by using a metal surface spinning at high speed. Complexity of design, as moving parts which are subjected to the high temperatures of pyrolysis, and high heat loss are the main disadvantages of this pyrolyzer [42]. In vacuum pyrolysis, feedstock is heated in a vacuum and the substrate residence time at the working temperature is limited as much as possible in order to minimize adverse secondary chemical reactions. This technology suffers from poor mass and heat transfer rates, and needs larger scale equipment [42].

Three key building blocks of lignocellulosic materials as cellulose, hemicelluloses and lignin have different thermal behaviors depending on heating rate and the presence of contaminants [44]. Fig. 5 [45] shows a typical mass loss rate of the reed decomposition performed through thermo-gravimetric analysis (TGA). Fig. 5A shows the total mass loss rate versus the temperature, while Fig. 5B indicates TGA data in terms of cellulose (almost 30%), hemicellulose (25%), and lignin (20%). The decomposition of first

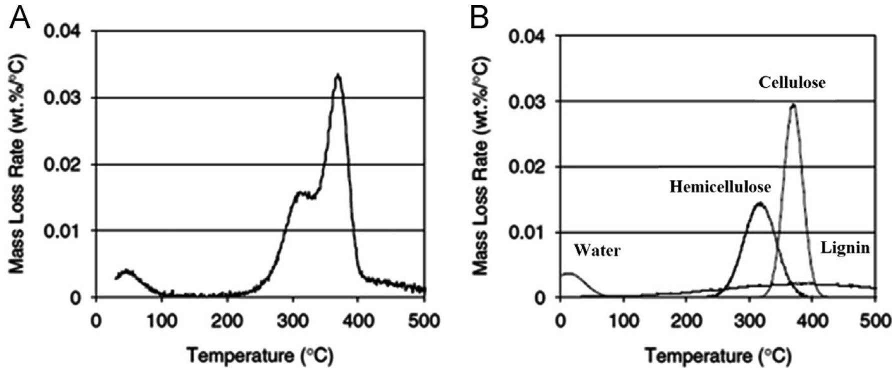


Fig. 5. Differential thermogravimetric analysis curve for Reed (A) and the differential plot interpreted in terms of hemicelluloses, cellulose and lignin (B) [45].

component, which is hemicelluloses, starts at about 220 °C and completed around 400 °C. Cellulose starts to decompose at approx. 310 °C and continued to 420 °C. Within this range, the produced vapor consists of non-condensable gas and condensable organic vapor. Lignin appears to be stable up to approx. 160 °C. Disruption of lignin structures through pyrolysis slowly continued and supposed to be extended up to approx. 800–900 °C. The conversion of lignin compound at temperature around 500 °C is probably limited to about 40%. The solid residue, produced from fast pyrolysis, is almost char. It is mainly derived by lignin (40 wt%) and some hemicelluloses (20 wt%) decomposition. From this TGA data, it can be concluded that bio-oil is mainly derived by cellulose decomposition while partially from hemicelluloses (about 80% conversion to oil and gas) and lignin (roughly 50% conversion to oil and gas). In biomass structure, covalent ester and ether bonds link lignin and hemicelluloses which cannot be easily released upon pyrolysis. In contrast, cellulose and hemicelluloses are linked by much weaker hydrogen bonds. Pyrolysis-derived char has an elemental composition close to lignin; this could be an indirect evidence for this hypothesis [46].

Depending on the reaction temperature and feed type, the pyrolysis of biomass can be either endothermic or exothermic. Pyrolysis of hemicellulosic materials is endothermic at temperature below about 450 °C and exothermic at higher temperatures. Different reactions and mechanisms involved in pyrolysis might be the reason [47]. Ball et al. [48] pointed out that the charring process was highly exothermal, whereas volatilization was endothermal.

The composition ranges of different available components in bio-oils are shown in Fig. 6 [33]. The compounds in bio-oil can vary by more than an order of magnitude. Bio-oil contains acids (acetic, propanoic), esters (methyl formate, butyrolactone, angelica lactone), alcohols (methanol, ethylene glycol, ethanol), ketones (acetone), aldehydes (acetaldehyde, formaldehyde, ethanedial), miscellaneous oxygenates (glycolaldehyde, acetol), sugars (1,6-anhydroglucose, acetol), furans (furfurol, HMF, furfural), phenols (phenol, DiOH benzene, methyl phenol, dimethyl phenol), guaiacols (isoeugenol, eugenol, 4-methyl guaiacol), and syringols (2,6-DiOMe phenol, syringaldehyde, propyl syringol). Depolymerization and fragmentation reactions of cellulose, hemicelluloses and lignin yield multi-component mixtures. Guaiacols and syringols are the example of lignin formed components, whereas sugars and furans are the example of cellulose and hemicellulose components, respectively. Decomposition of the miscellaneous oxygenates, sugars, and furans probably yield esters, acids, alcohols, ketones and aldehydes [33].

Bio-oil potentially can be used as a fuel, but there are some demerits associated with it as poor volatility, high viscosity, high corrosiveness, instability and cold flow problems [12].

Reactive oxygenated compounds in bio-oil such as ethers, aldehydes, ketons, acids and alcohols can react and form higher molecular weight species. These heavy compounds formation,

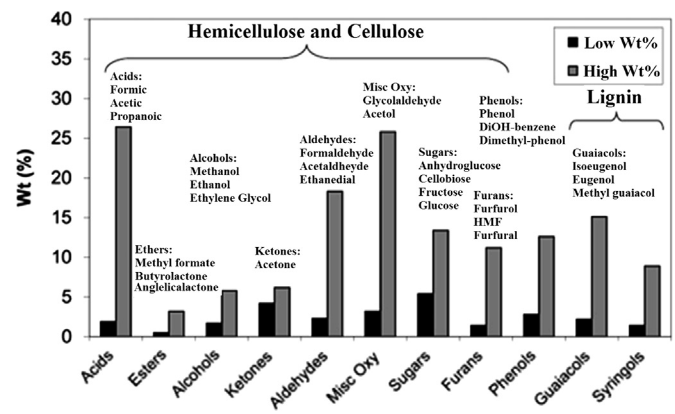


Fig. 6. Chemical composition of bio-oils. The graph also shows the most abundant molecules of each of the components and biomass fraction from which the components were derived [33].

which is accelerated by increasing temperature and under oxygen and UV light exposure, can induce problems such as increased viscosity and phase separation [33]. High contents of aldehydes and ketones in bio-oil make it hydrophilic and highly hydrated, which result in difficult elimination of water [49,50]. Carboxylic acids available in bio-oil lead to low pH value of 2–3. High bio-oil acidity makes it very corrosive especially at elevated temperature, which imposes more requirements on storage vessels material of construction and transportation [50].

These problems have limited bio-oil applications as an engine fuel due to its low heating value, presence of oxygenated compounds and high water contents. So, bio-oil must be upgraded or blended to be used in diesel engines [33].

4. Pyrolysis vapor upgrading using model compound approach

Bio-oil produced from the fast pyrolysis contains different types of oxygenated compound that make it unacceptable as transportation fuel component. One of the proposed solutions to stabilize bio-oil and reduce its oxygen content is to blend it with the feed of conventional hydrotreating processes [51], although the pyrolysis oil transportation and storage before its blending are still seriously complicated.

Another alternative is pyrolysis vapor upgrading before being condensate. The vapors need to pass through certain stabilizing catalytic processes. In this condition, pyrolysis vapor components undergo several reactions including cracking, aromatization, condensation, dehydration, decarbonylaation and decarboxylation. Through these reactions, oxygen can be removed in the form of CO, CO_2 and water. The catalysts could be selected as per process

Table 1
Effect of catalyst type on product distribution [54].

Type of catalyst	Temperature (°C)	Carrier gas	% Conversion	Product distribution (% yield)		
				Benzene	Toluene	Methane
HZSM-5	450	He	56.32	56.32	0.00	0.00
		H_2	54.23	54.23	0.00	0.00
3Ga/HZSM-5	450	He	55.80	55.80	0.00	0.00
		H_2	58.20	19.95	36.40	1.85
3Ga/HZSM-5	500	He	69.07	69.07	0.00	0.00
		H_2	70.22	20.42	43.71	6.09

requirement. To achieve this goal, as an initial step, fundamental knowledge on reaction pathway is required. This can be achieved through model compound investigations. The outcome of these studies can provide direction toward selection of proper process and catalysts [6,12].

The results of the model compound approach investigations to produce gasoline range molecules through conversion of small oxygenates (with minimum carbon loss), conversion of lignin-derived phenolics and conversion of sugar-derived compounds have been presented here. The catalyst deactivation, as one of the important problems associated with catalytic bio-oil upgrading, has been studied as well.

4.1. Conversion of small oxygenates (with minimum carbon loss)

Small oxygenated compounds available in pyrolysis vapor such as acids, aldehydes, alcohols and ketones can be catalytically deoxygenated through dehydration, decarbonylation and decarboxylation to stable fuel like molecules. Also, by utilizing the appropriate catalysts and relatively high reactivity of the oxygen functionalities (carboxylic, carbonyl, hydroxyl, and ketonic groups) bonds (like C–C) forming reactions, such as ketonization, etherification, aldol condensation and aromatization can be conducted. It means instead of oxygen functionalities elimination too early, utilize them as a potential for production of high carbon deoxygenated fuel components [31].

4.1.1. Deoxygenation of small aldehyde

Pyrolysis vapor/bio-oil stabilization can be achieved through oxygen removal from its oxygenated compounds. Light aldehydes are one of the abundant oxygenated chemical groups available in pyrolysis vapor/bio-oil [52,53]. Recently, Ausavasukhi et al. [54] investigated the catalytic deoxygenation of benzaldehyde over gallium-modified ZSM-5 zeolite. A continuous flow system was utilized to investigate the effects of reaction condition varations (Table 1) such as carrier gas (H_2 or He), reaction temperature, and water co-feeding. Toluene and benzene were the main products of benzaldehyde conversion over Ga/HZSM-5 catalyst. Direct deoxygenation over Brønsted acid sites yielded benzene, while toluene was only produced in the presence of H_2 over GaH_2^+ species (Fig. 7). These species were only generated under H_2 environment. In the absence of hydrogen, no toluene was yielded. Water co-feeding in the presence of Ga-modified HZSM-5 catalyst increased the benzene/toluene ratio.

In the other study done by Peralta et al. [55], deoxygenation of benzaldehyde to benzene and toluene over basic CsNaX and NaX zeolite catalysts was examined. The reaction was carried out at atmospheric pressure either in the presence of an inert gas or H_2 (Fig. 8). Highly basic catalyst with excess Cs content conducted direct decarbonylation of benzaldehyde to benzene. However,

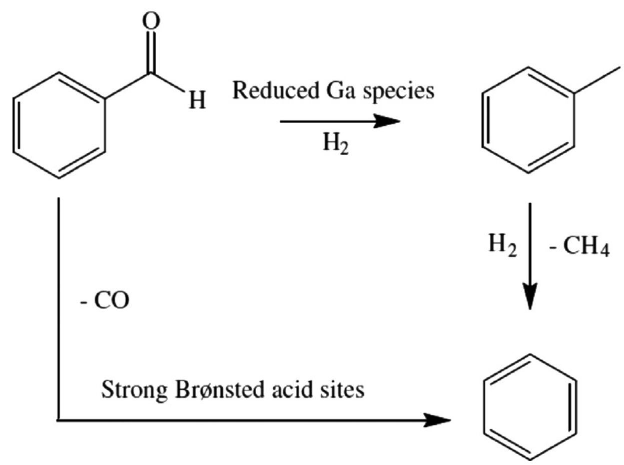


Fig. 7. Catalytic deoxygenation of benzaldehyde over Ga/HZSM-5 [54].

condensation of surface products took place in parallel with direct decarbonylation. Toluene and benzene were produced through decomposition of surface condensation products. Dissociation of H_2 from zeolite (with and without Cs) surface cleaned the catalyst by decreasing the residence time of intermediates on surface. So, accumulation of non-decomposable products that caused the catalyst deactivation was decreased. After H_2 dissociation, it participated in decomposition of condensation surface products and consequently primary toluene was formed. NaX and CsNaX catalysts did not show a high initial activity for direct decarbonylation, but they operated to decompose surface condensation products to benzene and toluene. A faster deactivation of NaX catalyst than CsNaX was observed due to the presence of residual acidity in it.

Comparing aforementioned ZSM-5 and NaX catalysts, incorporation of Ga and Cs, respectively, into the catalysts as well as reaction atmosphere changed the selectivity and yield toward benzene and toluene. High yield and selectivity toward benzene using Ga/HZSM-5 catalyst were observed under helium and water atmosphere whereas, CsNaX exhibited high yield and selectivity toward benzene under hydrogen atmosphere [54,55].

4.1.2. Condensation/ketonization/aromatization of small aldehyde

Stabilized bio-oil can be achieved by utilizing the molecules oxygen functionalities to facilitate C–C bonds formation via aldol condensation or ketonization [56,57]. Gangadharan et al. [57] selected propanal to investigate condensation reaction over $Ce_xZr_{1-x}O_2$ mixed oxides catalyst. This reaction modeled short aldehydes (found in bio-oil mixtures) conversion to gasoline range molecules. Different operating parameters comprising incorporation of acid and water in the feed were studied. The following

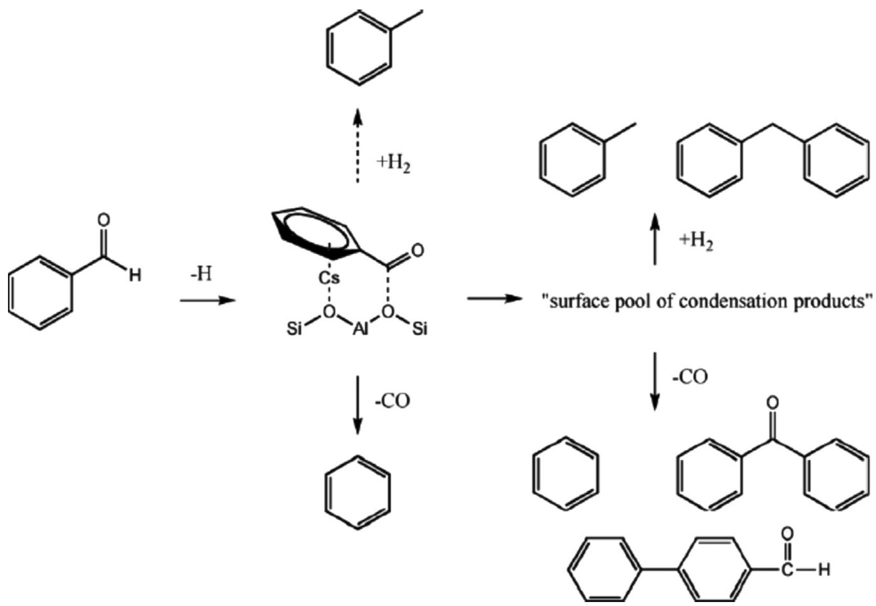


Fig. 8. Reaction pathway of benzaldehyde conversion to benzene and toluene on basic CsNaX and NaX catalysts [55].

important conclusions were drawn by them [57]: (a) Aldol condensation and ketonization were two pathways for propanal conversion to higher carbon chain oxygenates over ceria–zirconia catalyst. (b) Aldehyde aldol condensation reactions observed to be limited due to the competitive adsorption of acids presented in the feed. Presence of acid reduced the aldehyde adsorption and conversion. (c) Presence of water increased concentration of surface hydroxyl groups. It led to increase the catalyst activity by enhancing the formation of surface carboxylates. So, aldehyde ketonization was promoted, whereas aldol condensation was inhibited. (d) Presence of water improved the catalyst stability. (e) Cracking reaction was promoted to produce light oxygenates and light hydrocarbons in the presence of hydrogen. While the light hydrocarbon did not react further, the light oxygenates may be incorporated again to produce secondary products. (f) Shifting the balance of the acid–base properties of catalyst active sites could change the catalyst selectivity. Zr increasing favored formation of aldol products, while Ce increasing favored ketonization.

The reaction network shown in Fig. 9 was proposed based on mentioned results. The contribution of two major reactions (aldol condensation and ketonization) can be seen in the network, involving various condensation steps [57].

The investigations on the conversion of propanal over large (2–5 μm) and small (0.2–0.5 μm) crystallite HZSM-5 catalysts at 400 °C and atmospheric pressure were undertaken by Hoang et al. [58]. HZSM-5 crystallite size effects on the conversion of propanal to aromatics were investigated at rather mild conditions, 400 °C and atmospheric pressure. Due to the faster removal of products from small crystallite zeolite channels, which reduces production of coke precursors and coke, much slower catalyst deactivation was observed. Simultaneously, shorter diffusion path of small crystallites showed considerably less isomeration of xylene products to para-xylen than large crystallites.

In small crystallites, due to the shorter time for cracking before molecules diffuse out of zeolite, a higher fraction of C_9 aromatics was observed. C_9 aromatics were produced via propanal aldol condensation followed by cyclization. Therefore, the use of smaller crystallite HZSM-5 was suitable to improve production of fuel-like alkyl aromatics from light oxygenates at mild operating conditions [58]. On the other hand, in mixed oxide catalysts, increasing amount of zirconia led to a high yield of aromatic compounds due to an enhancement of the acid sites with zirconia increasing. The aromatization reactions were catalyzed by the acid sites [57].

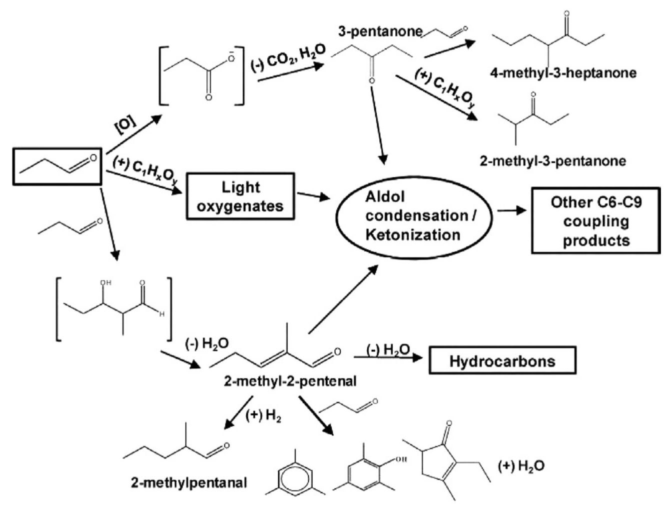


Fig. 9. Proposed reaction pathway for propanal conversion over $Ce_{0.5}Zr_{0.5}O_2$ [57].

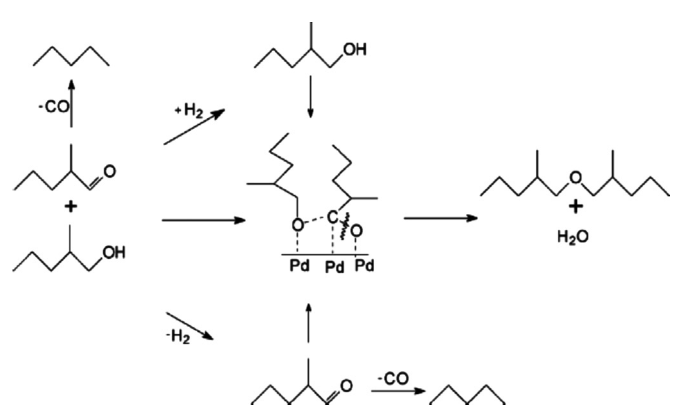


Fig. 10. Schematic reaction pathway of 2-methylpentanal on Pd catalyst [59].

4.1.3. Etherification of alcohols and aldehyde

Ethers as one of the potential fuel components are prepared from oxygenates that could be used either in diesel blends or gasoline. More recently, Pham et al. [59] investigated on selective production of di-alkyl ethers from etherification of alcohols and aldehydes on supported Pd catalysts. Fig. 10 indicates the proposed reaction pathway. High rates of ether formation could be achieved while both alkoxide and η^2-adsorbed species were available on the catalyst surface. Moreover, stoichiometric 1:1 ratio of aldehyde and alcohol was found to be the optimum. Larger sintered and annealed metal particles showed higher ether selectivity, but lower conversion. It is due to enhancement of ensembles needed for etherification.

4.1.4. Hydrodeoxygenation of small aldehyde

Generally, removal of oxygen from biomass originated molecules is essential to improve the fuel properties. Research octane number (RON), as a primary screening tool, is an important indicator to show if a molecule is potentially suitable to be used as fuel. Studies showed quite high octane numbers for the alcohols produced from 2-methyl-2-pentenal hydrogenation [60]. Pham et al. [61] studied hydrodeoxygenation and hydrogenation of 2-methyl-2-pentenal over platinum, palladium, and copper catalysts supported on precipitated silica in the temperature range of 200–400 °C. The catalyst's activity followed the order Pt > Pd > Cu. The reaction pathway has been shown in Fig. 11. The modeled reactions rate constants are tabulated in Table 2. The mentioned aldehyde is a molecule with the reactive functional groups of C=C and C=O which are typical in the oxygenated molecules available in bio-oil produced from pyrolysis. Hydrogenation activity of both C=C and C=O bonds over 0.5 wt% Pd and Pt catalysts was investigated. Strong hydrogenation of the C=C bond to form 2-methyl-pentanal was observed over 0.5 wt% Pd and Pt. Cu/SiO_2 (5 wt%) showed strong C=O initial hydrogenation activity to produce 2-methyl-2-pentenol. It then converted to 2-methyl-pentanol which was in equilibrium with 2-methyl-pentanal at higher conversion. As shown in Table 2, the relative hydrogenation rate of C=C versus C=O bond could be estimated by the ratio of k_1/k_2 for all catalysts. Considering Pt and Pd, this ratio was about 6, which indicated these metals were more selective for C=C hydrogenation. Conversely, much lower k_1/k_2 ratio for Cu (0.65) showed that this metal was less selective for this type of hydrogenation. C–C cleavage over Pt and Pd catalysts, which led to decarbonylation, became significant at higher temperature or higher ratio of catalyst to feed. C–O hydrogenolysis on Cu yielded 2-methyl-pentane as minor product at 200 °C. It became the major product over Cu, when temperature was increased to 400 °C. Due to the stability of 2-methyl-pentanol and its fairly good octane number, practically its production may be desirable over Cu catalyst at low temperature. Cu showed to be a desirable catalyst for total oxygen removal without carbon loss at higher temperatures. Despite higher Pt and Pd catalysts activity and their high selectivity for C=C hydrogenation, the loss of carbon through decarbonylation (yielding n-pentane and CO) was a disadvantage when the goal was conversion of small molecules to useful fuel range molecules with low carbon loss.

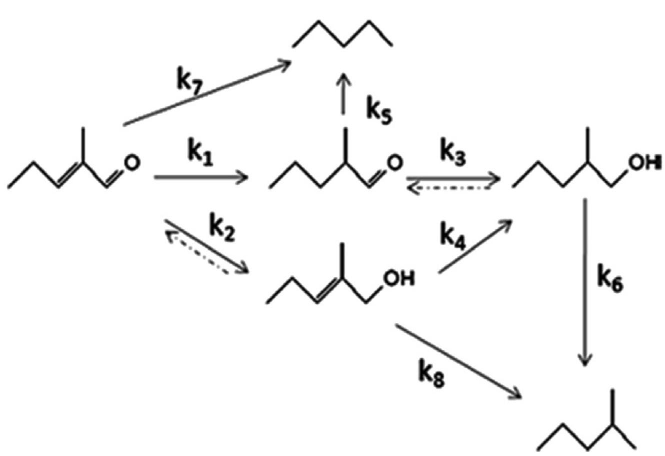


Fig. 11. Schematic conversion of 2-methyl-2-pentenal on Pt, Pd, and Cu (see Table 2) [61].

Table 2
First-order model rate constants (s^{-1}) [61].

Metal	Pt	Pd	Cu
Loading (wt%)	0.5%	0.5%	5%
k_1	2.65	0.2	0.01
k_2	0.41	0.04	0.01
k_3	0.29	0.44	0.00
k_4	19.64	1.12	0.09
k_5	0.29	0.02	0
k_6	0	0	0.01
k_7	0.93	0.10	0
k_8	0	0	0.02
k_1/k_2 ratio	6.5	5.67	0.65
k_7/k_1 ratio	0.35	0.47	0

4.1.5. Ketonization of small carboxylic acid

Small acid compounds such as propanoic acid and acetic acid are the most abundant oxygenated molecules available in bio-oil [62,63]. They not only cause corrosion problems, but also significantly reduce bio-oil stability.

In ketonization reaction, coupling of two carboxylic acid molecules produce ketone molecule while H_2O and CO_2 are eliminated. The produced ketones have potential to undergo further aldol condensation reactions (C–C coupling) to produce larger fuel-like hydrocarbons [64].

Recently, Yamada et al. [65] investigated the ketonization of acetic acid over a series of rare earth oxides (REOs) catalysts at 350 °C and under atmospheric pressure of nitrogen. Acetic acid conversion and selectivity over calcined (1000 °C) REOs catalysts at mentioned operating conditions have been shown in Table 3. The REOs catalysts such as La_2O_3, CeO_2, Pr_6O_{11}, and Nd_2O_3 showed the acetic acid conversion of ~38% to ~80% and the selectivity to acetone over 99.9%. Among fourteen studied REOs, Pr_6O_{11} showed the highest yield of 80% and Nd_2O_3 showed the highest selectivity of 100%. After acetic acid ketonization, several active REO catalysts were converted into an oxyacetate such as MO(AcO), M=La, Pr, and Nd (AcO indicates CH_3COO group). On the other hand, in the case of CeO_2, its surface was converted into acetate while the bulk structure of CeO_2 was retained during the ketonization. The specific surface area of CeO_2 and produced oxyacetate was proportional to acetone yield. It was concluded that, acetic acid ketonization over REOs catalysts continued on the surface of the oxyacetate like MO(AcO) via the

Table 3
Conversion and selectivity of acetic acid [65].

Rare earth oxides	Surface area ($m^2\,g^{-1}$)	Conversion (%)	Selectivity (mol%)			Acetone yield (%)
			Acetone	Acetic anhydride	Others	
La_2O_3	6.8	77.7	99.9	0.0	0.1	77.6
CeO_2	13.2	51.3	99.9	0.0	0.1	51.2
Pr_6O_{11}	4.6	80.1	99.9	0.0	0.1	80.0
Nd_2O_3	3.7	37.9	100	0.0	0.0	37.9

catalytic cycle between MO(AcO) and $M_2O(AcO)_4$ to produce acetone and CO_2 with the consumption of acetic acid.

4.1.6. Conversion of small alcohol to hydrocarbon

Bio-oil, which is a complex mixture of oxygenates, is immiscible with hydrocarbons and relatively unstable. Bio-oil deoxygenation and its transformation into a mixture of hydrocarbons over zeolite catalysts could guarantee compatibility with conventional gasoline [66]. Conversion of methanol to hydrocarbon (MTH) over H-ZSM-5 catalyst and the pertained reactions mechanism was studied by Bjorgen et al. [67]. They suggested two simultaneous mechanistic cycles run during the MTH reaction over H-ZSM-5 as follows: (a) formation of ethane/aromatics from methylbenzenes and then remethylation, and (b) ethylation/cracking cycle producing propene and higher alkenes. This can be observed in Fig. 12, where cycle I is an aromatics (toluene and trimethylbenzene)/ethane cycle and cycle II is an alkene-based cycle.

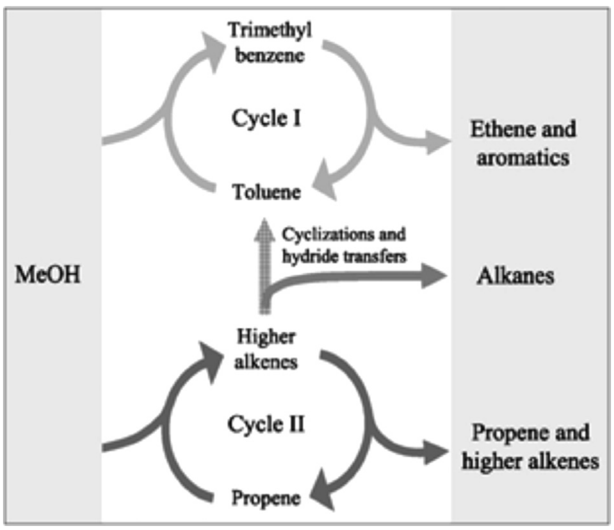


Fig. 12. Dual cycle concept for the conversion of methanol over H-ZSM-5 [67].

It may be asked whether two cycles (I and II) act independently or they are linked together in some manner. According to the results obtained by Bjorgen et al. [67], it was concluded that they could not run completely independent over the H-ZSM-5 catalyst.

Considering the mentioned mechanism, Ilias et al. [68] investigated on the selectivity of methanol-to-hydrocarbons conversion on H-ZSM-5 by co-processing olefin or aromatic compounds. They could control the composition of organic hydrocarbons and therefore manipulate the contributions of aromatic methylation and olefin cycles in MTH. Consequently, they could manage the selectivity of aromatics, C_4–C_7 aliphatics and ethene.

4.2. Conversion of lignin-derived phenolics

Selective cleavage of carbon–oxygen bonds of aromatics in lignin structure is a primary goal to unlocking the potential of lignocellulosic biomass to be used for biofuels production. Lignin is very difficult to upgrade due to its complex structure and recalcitrant nature. Furthermore, lignin comprises many phenolic moieties which can deactivate zeolite catalysts [69]. Anisol and guaiacol have been selected as model compound of lignin-derived phenolics for the investigations [32].

4.2.1. Anisole and guaiacol alkylation and deoxygenation

Zeolite catalysts have been widely studied for industrial alkylation and transalkylation of aromatic compounds [70]. Anisole, a typical component of bio-oil, conversion over HZSM-5 catalyst was studied by Zhu et al. [71]. It was selected as a model compound in catalyst and reaction evaluation for bio-oil upgrading. The kinetics studies (pseudo first-order kinetic model) showed that anisole (its methoxy group could provide interesting chemistry) could participate in both unimolecular and bimolecular reactions. Fig. 13 shows the reaction pathways. In order to quantify the contribution of each suggested reaction pathway and determine the dominant

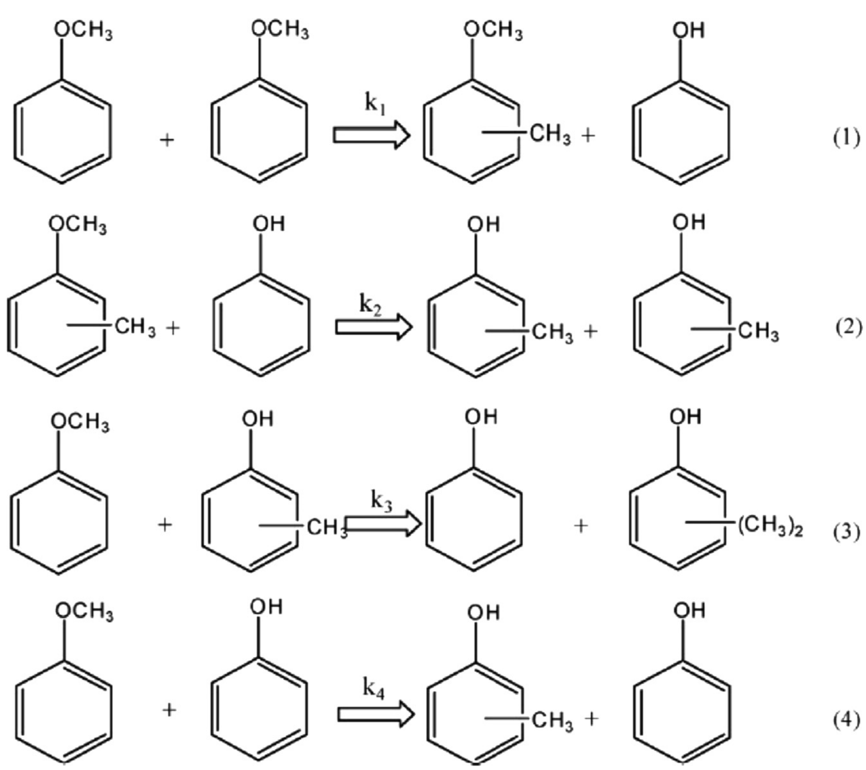


Fig. 13. Proposed major reaction pathways of anisole conversion over HZSM-5 (see Table 4) [71].

paths, a simple kinetic model was employed. Table 4 indicates the proposed reactions kinetics data. Bimolecular anisole transalkylation was observed to be dominated at low contact time and higher feed concentrations. At higher space time, secondary bimolecular reactions involving cresol, phenol and methylanisole became significant. Moreover, several parallel unimolecular reactions also took place. Shape selectivity was obvious in the distribution of different methylanisole isomers. Contrary, cresol isomers distribution was dominated by electrophilic substitution at low conversions and then by thermodynamic equilibrium. Conversion variation by reaction parameters such as reaction temperatures, space time, presence of hydrogen carrier, or catalyst deactivation gained the same product distribution. Contrary, product distribution drastically changed while water was added to the feed. Moreover, it was observed that the presence of water in the feed improved the zeolite catalyst activity without changing the stability, most likely due to the involvement of methoxy group hydrolysis.

In an earlier study, Zhu et al. [72] investigated the catalytic conversion of anisole over a bifunctional Pt/HBeta catalyst (Fig. 14) at 400 °C and atmospheric pressure. Comparison of bifunctional and monofunctional catalysts (Pt/SiO_2 and HBeta) indicated that acidic function (HBeta) catalyzed transalkylation from methoxy to the phenolic ring. Therefore, phenol, xylenols, and cresols were produced as the main products. On the other hand, Pt was observed to only catalyze demethylation, hydrodeoxygenation, and hydrogenation reactions, sequentially. Methyl transfer and hydrodeoxygenation reactions were accelerated by Pt addition to zeolite. These reactions took place with low hydrogen consumption and low carbon loss as methane. Rate of O–CH_3 cleavage was improved in the presence of metal and therefore enhanced the overall rate of methyl transfer reactions (catalyzed by Brønsted acid). Further, the stability of catalyst with moderate coke reduction was achieved due to metal addition to zeolite. Thus, it was concluded that, metal–zeolite properties optimization might be led to an efficient catalyst for the hydrodeoxygenation of phenolics rich bio-oils.

Recently, Prasomsri et al. [73] utilized flow and pulse reactors to examine the conversion of pure anisole and its mixtures with propylene, n-decane, benzene, or tetralin, over HY(Table 5) and HZSM-5 zeolites. Most of the studies were done on HY zeolites, which are known active components in fluid catalytic cracking (FCC) catalysts. During several dominant transalkylation steps, anisole conversion produced phenol, cresols, xylenols and methylanisoles as the main products over HY zeolite. As can be seen in Table 5, due to addition of anisole to tetralin (an effective hydrogen donor molecule), considerable effects on distribution of products were observed. Moreover, while pure anisole feeding showed fast catalyst deactivation due the coke deposition, the addition of tetralin to the feed caused lower quantities of carbon deposits and catalyst stability enhancement.

In the other investigation, Gonzalez-Borja et al. [74] carried out hydrodeoxygenation of anisole and guaiacol over monolithic Pt–Sn catalysts. Fig. 15 depicts deoxydenation and transalkylation/deoxygenation pathways of anisole and guaiacol over Pt–Sn/CNF/Inconel catalyst. Generally, monolithic catalysts have important advantages thanks to the generation of low pressure drop even at high reactants flow rate. So, they are a very good candidate for biomass pyrolysis vapor upgrading, where pyrolysis reactors operate at atmospheric condition. In this study, mono and bimetallic (Pt–Sn alloy) monoliths catalysts were synthesized and tested for the deoxygenation of guaiacol and anisole. Full deoxygenation of guaiacol and anisole was observed over both Pt–Sn/Inconel and Pt–Sn/CNF/Inconel (coated Inconel monoliths with in-situ-grown carbon nanofibers) catalysts. Phenol and benzene were the most important products obtained from the mentioned feeds over monolithic catalysts. Compared with the

Table 4
Proposed elementary reactions and fitted reaction rate constant k_i over HZSM-5 [71]. (An: anisole, Ph:phenol, MA: methylanisole, Cr: cresol, Xol: xylenol isomers.)

Number	Reaction	Fitted k_i	
		$\times 10^{-5}$ L mol^{-1} h^{-1}	h^{-1}
1	An + An → Ph + MA	0.032	
2	Ph + MA → Cr + Cr	0.25	
3	Cr + An → Ph + Xol	0.20	
4	Ph + An → Cr + Ph	0.16	
5	MA → Cr		0.093
6	Xol → Cr		0.38
7	Cr → Ph		0.37
8	An → Ph		0.093
9	An → Cr		0.35
10	MA → Xol		0
11	Cr + Cr → Ph + Xol	0	

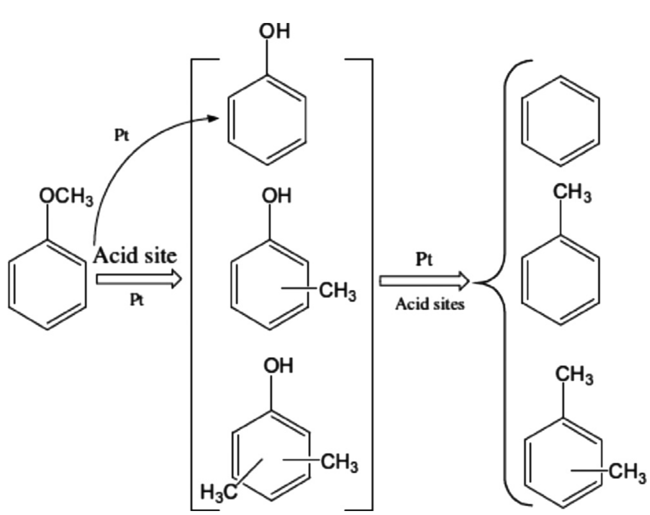


Fig. 14. Major reaction pathway for anisole conversion over 1% Pt/H-Beta. Reaction conditions: T=400 °C, P=1 atm, H_2/anisole=50, TOS=0.5 h [72].

Table 5
Product distributions from conversion of anisole and anisole–tetralin mixture (~50% tetralin) over HY zeolite. T=400 °C, P=1 atm under He [73].

Feed	Anisole		Anisole + tetralin	
	TOS = 0.5 h	TOS = 3.0 h	TOS = 0.5 h	TOS = 3.0 h
Conversion of anisol	83.6	13.9	100	100
Conversion of tetralin			98.4	96.6
Weight Percent at reactor outlet				
C_1–C_5	1.2	0.2	8.8	8.2
Anisole	16.4	86.1	0.0	0.0
Phenol	35.2	6.8	28.1	29.2
Methylanisoles	3.3	4.2	0.0	0.0
Cresols	26.4	1.4	12.5	13.1
Xylenols	17.5	1.3	2.8	2.8
Benzene	0.0	0.0	2.1	1.9
Toluene	0.0	0.0	3.5	3.0
Alkylbenzene	0.0	0.0	9.7	8.8
Tetralin	0.0	0.0	0.8	1.7
Naphthalene	0.0	0.0	20.0	19.9
Alkylnaphthalene	0.0	0.0	9.9	9.5
Heavies	0.0	0.0	1.8	1.9
Selectivity of anisole product (wt%)				
Methane	1.4	1.4	2.8	1.1
Phenol	42.1	48.9	63.7	64.0
Methylanisoles	3.9	30.2	0.0	0.0
Cresols	31.6	10.1	27.4	28.7
Xylenols	20.9	9.4	6.1	6.1

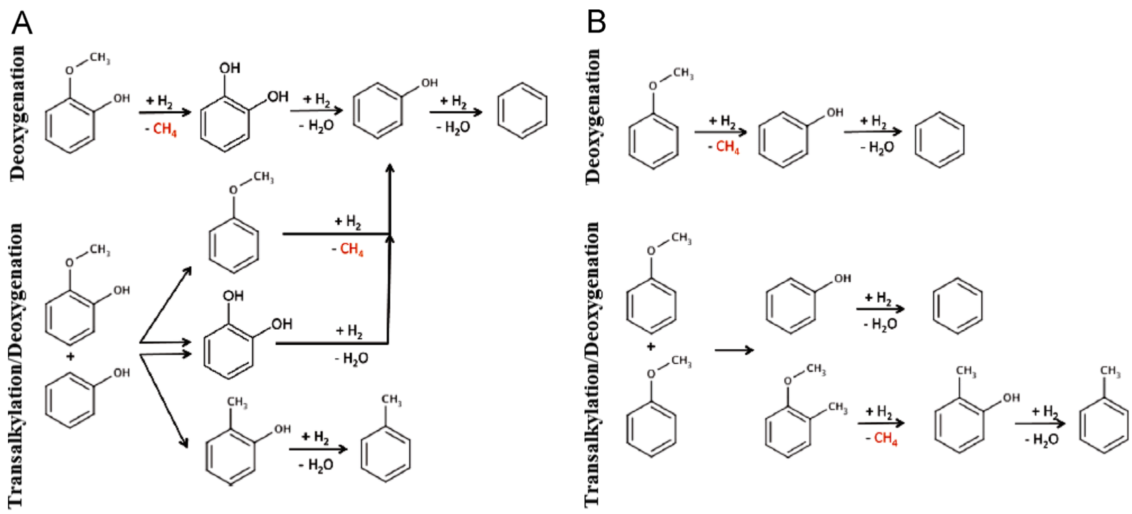


Fig. 15. Reaction pathways for guaiacol (A) and anisole (B) deoxygenation on the Pt Sn/CNF/Inconel catalyst [74].

monoliths without coating, CNFs coated catalysts increased monoliths surface area more than 10 times, which provided higher metal uptake during active-phase incorporation. Although, Pt–Sn/CNF/Inconel monolith was found to be a promising catalyst for the upgrading of pyrolysis bio-oil, the catalyst deactivation needed to be improved.

As explained above, incorporation of Pt and Pt–Sn metals into HBeta and CNF/Inconel monolith catalysts, respectively, could improve catalysts selectivity and stability [72,74]. Although, in the case of HY zeolite, these improvements of catalyst could be achieved by addition of a hydrogen donor molecule (like tetralin) to the feed [73].

4.3. Conversion of sugar-derived compounds

Among numerous oxygenated compounds commonly found in bio-oil, furfural was selected as a model for sugar derived compounds. These compounds have high reactivity and needed to be catalytically deoxygenated to improve bio-oil storage stability, boiling point range, and water solubility [75]. Furfural is produced both during the dehydration of sugars and cellulose pyrolysis.

4.3.1. Furfural decarbonylation, hydrogenation and hydrodeoxygenation

Conversion of aldehydes, one of undesirable reactive components available in bio-oil, to alcohols has been studied over different metal based catalysts by several researchers [54,76]. Group Ib metals like Cu could catalyze conversion of furfural to furfuryl alcohol, but decarbonylation was only observed with high metal loading at high temperature [77]. In contrast, metals like Pd from group VIII, indicated much higher activity for furfural decarbonylation [78]. Sitthisa et al. [79] carried out the conversion of furfural under hydrogen and over silica-supported monometallic Pd and bimetallic Pd–Cu catalysts. Fig. 16 shows two parallel routes in furfural conversion over Pd catalyst. First, its decarbonylation to furan and then hydrogenation to terahydrofuran (THF), and second, furfural hydrogenation to furfuryl alcohol and then hydrogenation to tetrahydro furfuryl alcohol. Studies on furfural deoxygenation reactions over Pd and Pd–Cu catalysts concluded the following: (a) Decarbonylation of furfural as an aldehyde over Pd catalyst was the dominant reaction even at low space time (*W*/*F*=catalyst mass/mass flow rate of reactant). This was due to the decomposition of an acyl intermediate into CO and hydrocarbons at higher temperatures. In the presence of Pd catalyst, high decarbonylation/hydrogenation ratio was observed. (b) Furfural hydrogenation probably occurred via a stable hydroxyalkyl intermediate. (c) Pd–Cu alloy catalyst was made through incorporation of Cu on to Pd/SiO_2 catalyst. Due to different electronic structure of alloy from pure Pd, the formation of the side-on η^2-(C–O) aldehyde species were less stable on Pd–Cu than on pure Pd. So, the formation of the acyl intermediate likely decreased and it led to reduction of decarbonylation rate on Pd–Cu catalysts, whereas the hydrogenation rate was increased.

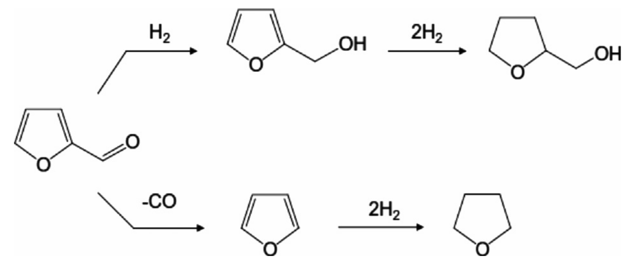


Fig. 16. Major reactions pathway for furfural conversion over Pd catalyst [79].

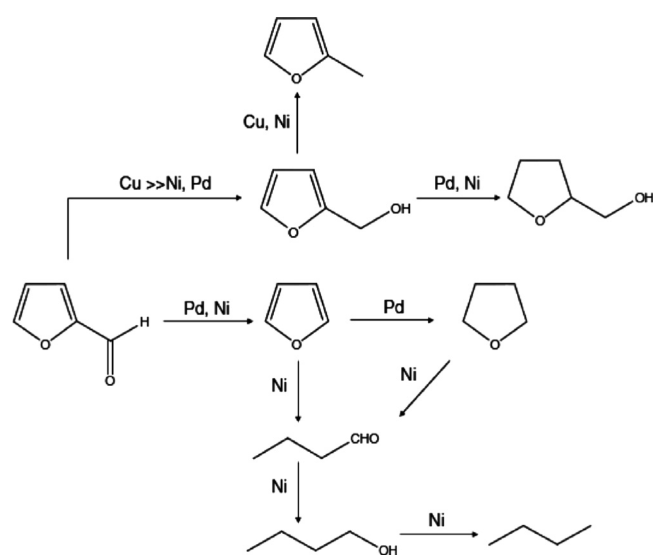


Fig. 17. Possible reaction pathways for furfural conversion over Cu, Pd and Ni catalysts [75].

The hydrodeoxygenation of furfural over three various metal catalysts, Cu, Pd and Ni supported on SiO_2 was carried out by Sitthisa et al. [75]. The catalysts studies were performed in a

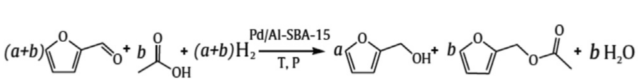
continuous-flow reactor under hydrogen atmosphere and temperature range of 210–290 °C. The products distribution was a strong function of used metal catalyst. Fig. 17 indicates the possible furfural conversion reaction pathways and shows which paths are favored over Pd, Ni and Cu catalysts. The reactions over silica supported Cu, Pd, and Ni catalysts showed different products distribution in terms of molecular interactions with the metal surface as following: (a) Furfuryl alcohol was produced over Cu catalyst via carbonyl group hydrogenation. This was due to preferred adsorption on Cu, η^1 (O)–aldehyde. Since furan ring adsorption was not favored on Cu surface, no products from furanyl ring activation was observed. (b) Due to the formation of acyl surface spices, Pd catalyst yielded decarbonylation products. Since there was a strong interaction between Pd and ring, products yielded from ring hydrogenation were observed. (c) Ni showed a product distribution similar to that of Pd. Due to furan stronger interaction with Ni surface, it further reacted with hydrogen, and thus formed ring opening products.

4.3.2. Hydrogenation–esterification of furfural

Bio-oil mostly comprises furan and acid compounds with the approx. weight percentages of 26% and 12%, respectively [33]. The major abundant acid and furan components in bio-oil are acetic acid and furfural, respectively [33]. They are undesirable components in bio-oil due to their high corrosiveness and reactivity [50,80,81]. The desired combustible products can be stable oxygenates such as alcohols and esters. So, reaction of acids and aldehydes can lower bio-oil acidity and improve its stability.

Furfural and other furan derivatives are prone to deactivating catalysts significantly; therefore it is quite a serious challenge to convert available furfural in crude bio-oil to a stable compound. So, furfural and acetic acid were selected as model compounds to be studied in this investigation. Yu et al. [80] evaluated Al-SBA-15 and $Al_2(SiO_3)_3$ supported palladium bifunctional catalysts for one-step hydrogenation–esterification (OHE) of furfural and acetic acid as a model reaction for bio-oil upgrading. The OHE reaction of furfural and acetic acid is illustrated in Eq. (1) [80].

The results of their research were summarized as following: (a) Al-SBA-15 showed better performance as supports of bifunctional catalysts than $Al_2(SiO_3)_3$. OHE of furfural and acetic acid in the presence of Al-SBA-15 catalyst (support) yielded desired products. (b) Esterification of furfuryl alcohol and acetic acid was favored by Al-SBA-15 with medium acidity. So, it could benefit the one-step hydrogenation–esterification of furfural and acetic acid. (c) A synergistic effect between acid and metal sites for the OHE reaction over composite bifunctional catalysts of 5% Pd/$Al_2(SiO_3)_3$ or 5% Pd/Al-SBA-15 was observed compared with the mixed bifunctional catalysts. (d) The OHE reaction of furfural and acetic acid was viable over either composite bifunctional (5% Pd/Al-SBA-15) or mixed bifunctional (5% Pd/C+Al-SBA-15) catalysts, attributed to the performing of hydrogenation and esterification reactions. OHE reaction on mesoporous materials supported metal as catalysts was a more efficient route for catalytic upgrading of real bio-oil, since there is greater accessibility of large molecules to acid sites in Al-SBA-15 relative to $Al_2(SiO_3)_3$.



(1)

Although in this study one-step hydrogenation–esterification reaction was carried out at high pressure, but it could give an interesting idea for further investigation on performing the similar reactions at atmospheric condition, which would be desirable for in-situ biomass vapor upgrading in an integrated process.

Table 6 shows the summary of the different model compound approach investigations that have been surveyed under different catalyst types and reaction conditions.

4.4. Catalyst deactivation

The catalyst deactivation is one of the major problems in catalytic bio-oil upgrading. It is proposed that the deactivation is caused by not only coke formation, but also the strong adsorption of the oxygenate compounds on the surface of catalyst supports. It is noted that, this effect is much more prominent on the aluminosilicate-type of catalysts, which contain acid sites [82,83].

Model compound studies may reasonably propose some efficient catalyst for certain bio-oil component upgrading, but the situation tends to be much more complicated while the entire mixture of pyrolysis oil compounds is fed on a given catalyst. The presence of some impurities like alkalis, as well as S- and N-containing compounds makes the task even more difficult. Among all bio-oil components, lignin derived phenolics, those with multiple oxygen functionalities (–OH, –OCH_3, C=O), are the most highly deactivating and make greatest challenges of bio-oil upgrading [84].

The presented oxygen contents in bio-oil derived compounds, mostly phenolics, strongly interact with active acid sites of catalysts and deactivate them. Anisole and guaiacol, among those phenolic compounds in bio-oils, have been selected as model compounds to investigate catalysts behavior. They exhibited highly competitive adsorption and rapid catalyst deactivation. A highest heat of adsorption of guaiacol has been reported [74].

Popov et al. [84] investigated the influence of acid–base properties of oxides on the adsorption modes of phenolic type molecules. They observed that doubly anchored phenates were created from guaiacol chemisorptions on alumina while phenol and anisole adsorption on catalyst made monoanchored species. Besides phenolic compounds, which speeded up catalysts deactivation through strong adsorption, the presence of oligomers, char particles, and inorganics typically found in pyrolysis oil greatly accelerated deactivation. It is not still clear whether the presence of heavy oligomers is due to phenolics and other components re-condensation as the vapors condense or they are even present in the original vapor phase. If their presence is not considerable in the original vapor phase, methods such as catalytic pyrolysis and upgrading of vapors might greatly stabilize the most reactive components and improve catalyst life [31,84].

The conversion of anisole on HY zeolite, which yielded phenol, cresols, xylenols and methylanisoles as main products during several transalkylation steps, was performed by Prasomsri et al. [73]. Significant catalyst deactivation under reaction conditions was caused by strong adsorption of phenolic compounds on catalyst and coke formation. Contrary to coke formation which was irreversible, phenolic compounds adsorption was reversible and could be minimized by incorporation of molecules such as tetralin with high H-transfer capacity. Anisol conversion and coke formation reduction was effectively improved by tetralin (or other H-donors) co-feeding. Other hydrocarbons with a weaker H-transfer capacity like n-decane, benzene and propylene were observed to have respectively lower, negligible and even detrimental effect on catalyst activity.

As indicated in Fig. 18, in the case of anisole co-feeding with tetralin, a significant increase in anisole conversion from ~20% to ~100% was observed as a function of time on stream (TOS). In this case, the roles of teratin were (a) H-transmission and removal of the species that deactivate the catalyst surface. (b) Starting the non-dissociative bimolecular transalkylation on the open structure of HY zeolite [73].

In Borja et al. [74] research, catalytic species (Pt, Sn, and bimetallic Pt–Sn) were impregnated on low-surface-area Inconel monoliths coated with in-situ-grown carbon nanofibers (CNFs).

Table 6
Summary of model compounds used in bio-oil upgrading research under different catalysts and reaction conditions.

Feed	Product	Reaction type	Catalyst	Operating conditions	Yield (Y) and selectivity (S) (%)	Ref.
Benzaldehyde	Benzene–Toluene	Deoxygenation–decarbonylation	Ga/HZSM-5	T=500 °C P=1 atm	$Y^{(b)}_{Benzene}=69.07$ $S^{(b)}_{Benzene}=100$	[54]
Benzaldehyde	Benzene–Toluene	Deoxygenation, decarbonylation	Basic CsNaX, NaX zeolite	T=500 °C P=1 atm	$Y^{(c)}_{Benzene}=70$ $S^{(c)}_{Benzene}$77.8 $Y^{(c)}_{Toluene}=20$ $S^{(c)}_{Toluene}=22.2$	[55]
Propanal	C_6–C_9	Aldol condensation, ketonization	Ce_XZr_{1-X} O_2 mixed oxides	T=400°C P=1 atm	$Y^{(d)}=\sim35$ $S^{(d)}=\sim40$	[57]
Propanal	Aromatics	Aldol condensation, Aromatization	Crystallite HZSM-5	T=400 °C P=1 atm	$Y^{(e)}=\sim50$ $S^{(e)}=\sim52$	[58]
Aldehydes–alcohols	Di-alkyl ethers	Etherification	Supported Pd catalysts	T=125 °C P=1 atm	$Y^{(f)}$=11.9 $S^{(f)}$=50.1	[59]
2-Methyl-2-pentenal	2-Methyl-2-pentane 2-Methyl-2-pentanol	Hydrodeoxygenation and hydrogenation	Platinum, palladium, and copper on silica	T=200 °C P=1 atm	$Y^{(g)}_{2-Me-2-pentanol}=70$ $S^{(g)}_{2-Me-2-pentanol}=70$	[61]
Acetic acid	Acetone	Ketonization	Rare earth oxides (REOs) such as La_2O_3, CeO_2, Pr_6O_{11}, and Nd_2O_3	T=350 °C P=1 atm	$Y^{(h)}$=99.9–100 $S^{(h)}$=37.9 (Nd_2O_3)–80 (Pr_6O_{11})	[65]
Methanol	Hydrocarbons, aromatics	Deoxygenation, aromatization	HZSM-5	T=290–390 °C $P^{(a)}$=1 atm	$Y^{(i)}_{C6+}=20.7$ $S^{(i)}_{C6+}=28.4$	[67,68]
Anisole	Cresol, phenol and methylanisole	Transalkylation	HZSM-5	T=400 °C P=1 atm	$Y^{(j)}$=6 (MA), 32 (Cr), 33 (Ph) $S^{(j)}$=6.7 (MA), 35.5 (Cr), 36.7 (Ph)	[71]
Anisole	Benzene, alkylbenzenes	Transalkylation–hydrodeoxygenation	Pt/HBeta	T=400 °C P=1 atm	$Y^{(k)}=S$=51.2 (Bn), 27.6 (Tn), 10.6 (Xn)	[72]
Anisole and tetralin	Phenol, cresols, xylenols and methylanisoles	Transalkylation	HY–HZSM-5	T=400 °C P=1 atm	$Y^{(l)}$=29.2 (Ph), 13.1 (Cr), 2.8 (Xnol) $S^{(l)}$=64 (Ph), 28.7 (Cr), 6.1 (Xnol)	[73]
Anisol–guaiacol	Toluene, benzene, phenols	Deoxygenation–transalkylation	Pt–Sn/Inconel Pt–Sn/CNF/Inconel	T=400 °C P=1 atm	An: $Y^{(m)}$=12 (Ph), 35 (Bn), 3 (Tn), $S^{(m)}$=21.8 (Ph), 63.6 (Bn), 5.4 (Tn) Gu: $Y^{(m)}$=70 (Ph), 10 (Bn), 2 (Tn), $S^{(m)}$=71.4 (Ph), 10.2 (Bn), 2 (Tn)	[74]
Furfural	Furan–C_4	Hydrodeoxygenation	Metal catalysts, Cu, Pd on SiO_2	T=210–290 °C P=1 atm	$Y^{(n)}=S^{(n)}$=50 (furan), 24 (butane)	[75]
Furfural-2-methylpentanal	THF, furfuryl alcohol, furan, ether, C_5, 2-methylpentanol	Hydrogenation, decarbonylation, etherification	Pd, Pd–Cu on SiO_2	T=125–250 °C P=1 atm	Furf: $Y^{(o)}$=16 (Fu), 8 (FOL), 2.5 (THF) $S^{(o)}$=58 (Fu), 28 (FOL), 9 (THF) MP: $Y^{(o)}$=15 (Et), 10 (MPOL), 4 (C_5), $S^{(o)}$=53 (Et), 36 (MPOL), 14 (C_5)	[79]
Furfural and acetic acid	Furfuryl alcohol, ester (furfuryl acetate)	Hydrogenation–esterification (OHE)	Al-SBA-15 and Al_2 $(SiO_3)_3$ supported palladium	T=150 °C P= 20 bar	$Y^{(p)}$=43.2 (FOL),12.8 (FA), $S^{(p)}$=61.8 (FOL), 18.2 (FA)	[80]

(a) Feed partial pressure in He carrier gas at 20 °C is 13 kPa; (b) W/F=100 g h/mol, carrier gas=He; (c) W/F=942 g h/mol, carrier gas=H_2, TOS=400 min, catalyst: CsNaX; (d) W/F=1 h under H_2; (e) small crystalline HZSM-5 (Si/Al=45) catalyst, TOS=30 min, W/F=0.2 h under H_2; (f) 16 wt% Pd/SiO_2 catalyst, W/F=1 h under H_2; (g) on 5 wt% Cu/SiO_2 catalyst at W/F=1 h, H_2: feed ratio=12:1; (h) conversion and selectivity were averaged in the initial 2.5 h, W/F=0.187 g h cm^{-3};(i) reaction temperature T=350 °C; (j) MA: methylanisole, Cr: cresol, Ph: phenol, W/F=0.5 h, carrier gas=He; (k) Bn: benzene, Tn: toluene, Xn: xylene, W/F=0.33 h on 1% Pt/HBeta catalyst; (l) Ph: phenol, Cr: cresols, Xnol: xylenols, anisole–tetralin mixture (50% tetralin) over HY zeolite catalyst, W/F=0.42 h, TOS=3 h; (m) An: anisol, Gu: guaiacol, Ph: phenol, Bn: benzene, Tn: toluene, TOS=45 min, $(W/F)_{An}$=1.3 h, $(W/F)_{Gu}$=1 h; (n) T=250 °C, W/F=9.6 gcat/(mol/h), H_2/feed ratio=25, TOS=15 min; (o) Furf=furfural, Fu=furan, FOL=furfuryl alcohol, Et=ether, MP=2-methylpentanal, MPOL=2-methyl-pentanol; Y&S (Furf): Pd–Cu/SiO_2 (0.5% Cu) catalyst, W/F=0.1 h, Temp=230 °C, H_2/feed=25, TOS=15 min; Y&S (MP): Pd–Cu/SiO_2 (2.5% Cu) catalyst, W/F=3 h, Temp=125 °C, H_2/feed=12, TOS=15 min; (p) FA: furfuryl acetate, FOL: furfuryl alcohol.

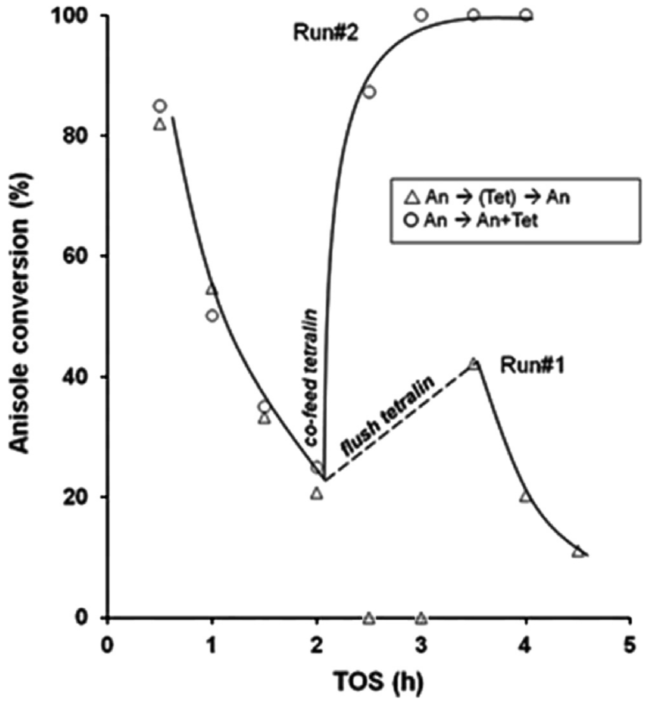


Fig. 18. Effect of co-fed tetralin on anisole conversion over the HY zeolite. Reaction conditions: W/F=0.42 h (wrt anisole for co-feed reaction), co-feed concentration=~50%, T=400 °C, P=1 atm He [73].

These monoliths were tested for the deoxygenation of guaiacol and anisole, two lignin derived pyrolysis compounds present in bio-oil. Phenol and benzene were the main products of guaiacol and anisole reactions on monolithic catalysts. CNFs coating, provided high surface area and anchoring sites for Pt and Sn active spices. It consequently improved the yield of desired products. The behavior of platinum and palladium catalysts supported on both carbon nanofiber (CNF)-coated monoliths and alumina washcoated monoliths were studied. The following was found: (a) Surface area was doubled when CNFs were grown. (b) Water adsorption on the support caused reduction of catalyst deactivation due to the higher hydrophobicity of carbon compared to alumina.

Graça et al. [85] studied the n-heptane reactions over zeolites catalysts mixtures to understand the influence of phenol on conversion and the products distribution. They also investigated the effect of each zeolite on the pure n-heptane transformation and on the phenol adsorption.

Data found from the zeolites mixtures were compared to the pure HY and HZSM-5 zeolites. Regarding pure zeolites, phenol increased the zeolites mixtures deactivation due to the high carbon accumulation. However, mixing the HY and HZSM-5 zeolites provided a further resistance to phenol poisoning. An initial adsorption of phenol on HY reduced its detrimental effects over HZSM-5 zeolite. The products distributions analysis in the presence of phenol and HY+HZSM-5 zeolites mixtures also indicated an initial preferential adsorption of phenol on the HY zeolite. It led to an increase of the paraffins/olefins molar ratio and the amount of branched species on the effluent, as observed for the pure HY zeolite.

Investigations on the bio-oil model compounds comprising phenols, aldehydes, acids, alcohols and ketones over HZSM-5 catalyst indicated that deposition of coke is highly depending on operating conditions like space time, reaction medium and temperature. Increase of water content and space time caused mitigation of coke deposition. Further, at lower temperature, less coke contents were observed [86,87]. High reaction temperature could cause cracking and condensation reactions promotion, resulting in coke contents enhancement [88].

During methanol to hydrocarbon (MTH) process, HZSM-5 showed rapid deactivation due to the deposition of carbonaceous residue (coke) on the catalyst and hindering the reactants to access the active sites [89]. Investigations done by Srivastava et al. [90] reported that HZSM-5 zeolite having hierarchical MFI pore topology was deactivated at much slower rate compared to conventional MFI zeolite (HZSM-5). Further, Kim et al. [91] showed that the generation of secondary mesoporosity within MFI zeolite could increase the catalyst lifetime by three times. Their results indicated that in the case of mesoporous zeolite, the coke mainly appeared on mesoporous walls. On the other hand, in the case of microporous zeolites, the coke was mainly deposited inside micropores. They concluded that, facile diffusion of coke precursors attributed to their short diffusion path length could probably improve the catalyst lifetime.

Novel ideas are being explored to minimize the catalyst deactivation complexity while whole real bio-oil mixture is treated. This challenging area will open the doors toward new research opportunities. Following examples [31] could be evidences for the carried out attempts in this regard. (a) The combination of hydrolysis with catalytic pyrolysis was studied by Jae et al. [92]. This method separated the products into different streams which were enriched in any of the mentioned families. Successive catalytic refining steps to focus on the required specific chemistry, like C–C bond formation and C–O bond cleavage, were done by the multistage method. (b) A liquid phase catalytic depolymerization method for lignin was dedicated by Roberts et al. [93], in which phenolic monomers as the only primary products were produced through base-catalyzed hydrolysis, while oligomers were formed in the secondary re-condensation steps. To inhibit oligomerization, boric acid was used to suppress condensation reactions.

5. Proposed catalysts and process for bio-oil upgrading

The main technical challenge on bio-oil stabilization and development is to design catalytic process and catalysts that fulfill deoxygenation while minimizing hydrogen consumption and maximize carbon efficiency. The model compound approach, as a fundamental key tool, has been utilized to identify the catalysts behavior and the relevant chemical process for bio-oil improvement.

5.1. Proposed pyrolysis–upgrading integrated process

High-pressure pyrolysis product treatment cannot be easily integrated with conventional fast pyrolysis atmospheric reactors. The only option is therefore to somehow isolate two process means condense the pyrolysis vapors and then feed the liquid bio-oil to the high pressure units. The great challenge in doing this in large scale is the low chemical and thermal stability of bio-oil. A more desirable option would be to directly feed the vapors coming out of the pyrolysis unit into upgrading reactors [74].

Based on the comprehensive investigation done on model compound approach research and following to catalysts selections, an integrated process for biomass pyrolysis and upgrading has been suggested (Fig. 19). Fluid bed fast pyrolysis of biomass was selected due to the merits associated with this type of process mentioned earlier in the context. As depicted in Fig. 20, pretreated milled biomass is introduced to the pyrolyzer (R01) through a screw feeder. The preheated nitrogen gas provides the fluidization condition during pyrolysis. The exit vapor from R01 after passing from two CY01 and CY02 cyclones and following to the separation of remaining chars is directed to Catalytic Vapor Upgrading Package (PK01) where bio-oil vapor is upgraded during cascade

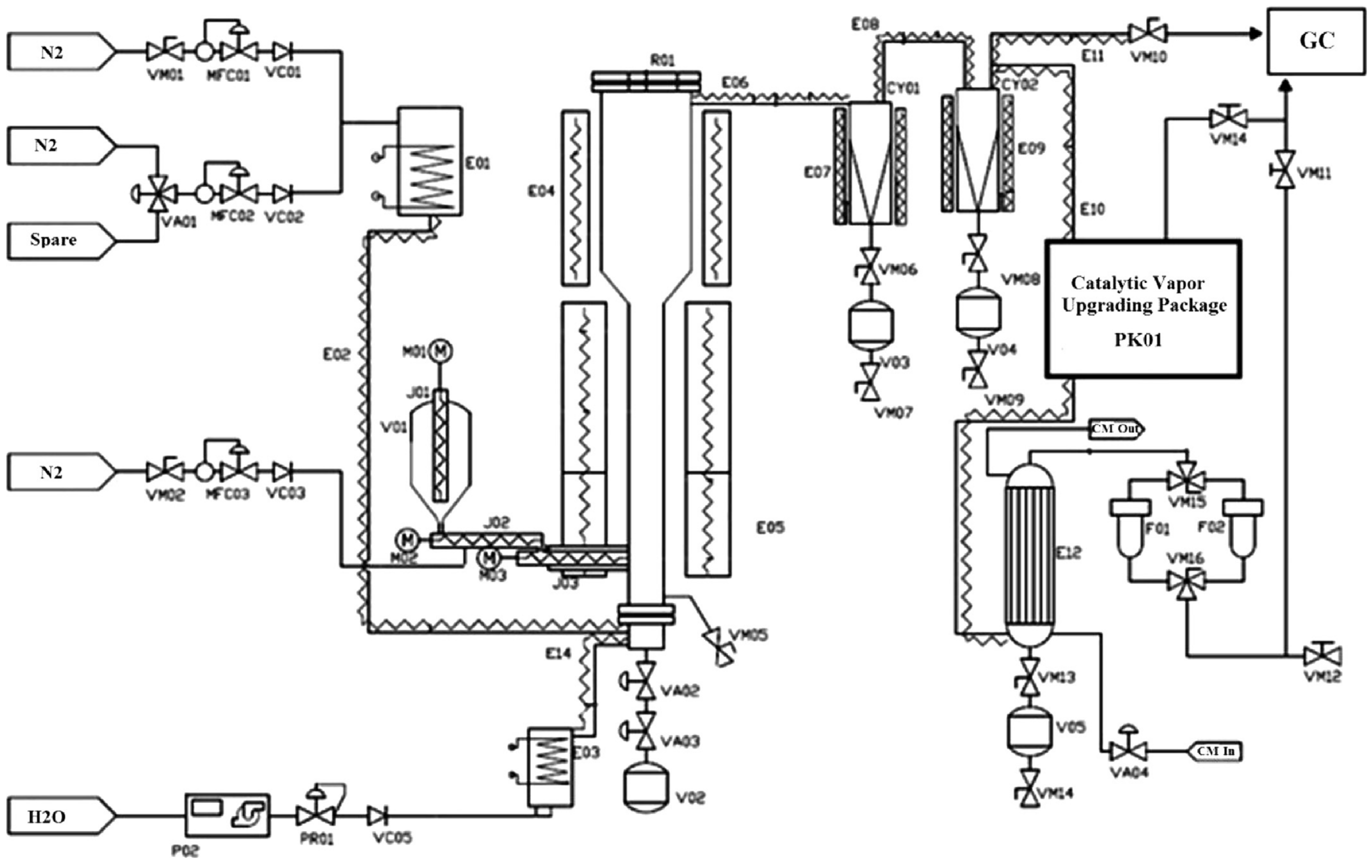


Fig. 19. Suggested biomass pyrolysis and vapor phase bio-oil upgrading integrated process (see PK01 detail in Fig. 20) (E: Exchanger, V: Vessel, MFC: Mass Flow Controller, VA–VC–VA: Valve, F: filter, R: Pyrolyzer, CY: Cyclone, J: Screw Feeder, M: Electromotor, P: Pump, GC: Online Gas Chromatograph).

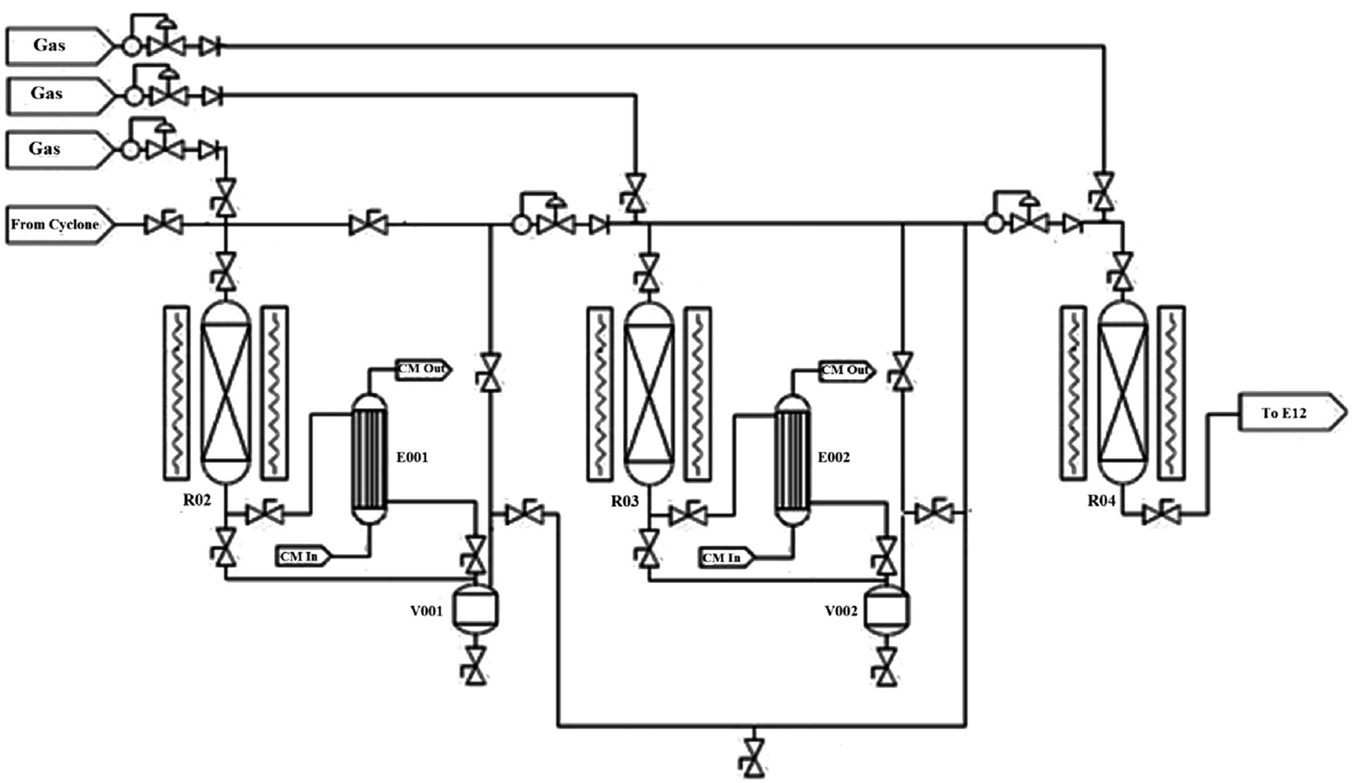


Fig. 20. Catalytic vapor upgrading package (PK01) detail (see Fig. 19) (R: Fixed bed reactor, V: Vessel, E: Exchanger).

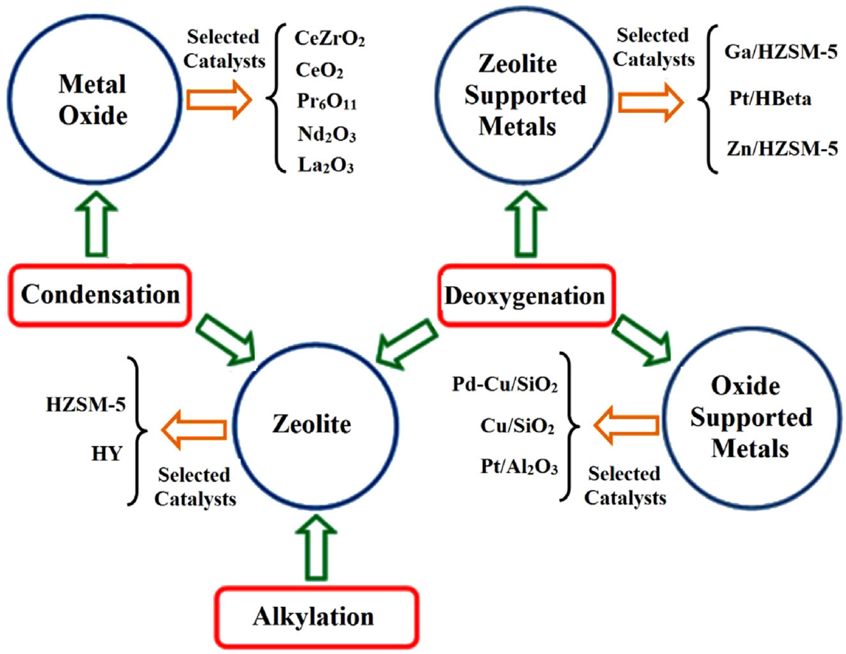


Fig. 21. Selected catalysts from different catalysts' groups for various chemical upgrading reactions.

catalytic process. The updated bio-oil vapor after condensation in E12 is collected in V05. The vapor streams from pyrolyzer, PK01 and E12 off gas can be analyzed by on line Gas Chromatograph (GC). Fig. 20 shows detail of catalytic vapor upgrading package (PK 01). The said package is equipped with three fixed bed reactors of R02, R03 and R04. For the possibility of temperature adjustment in cascade fixed bed reactors, E001 and E002 have been considered. The design of catalytic vapor upgrading reactors is flexible enough for different reactors' configurations. It can facilitate the conditions for the different research on in-situ bio-oil upgrading, which is still immature.

5.2. Catalysts selection

As the outcome of done survey, Fig. 21 at a glance shows simply the different catalysts' classes suggested for each individual reaction type. As indicated in Fig. 21, zeolite catalysts are prone to accomplish varieties of reactions comprising deoxygenation, condensation and alkylation. Deoxygenation, as one of the crucial reactions to achieve fuel-like molecules, can be performed by different types of catalysts, including zeolites, zeolite supported metals and oxide supported metals. According to the done survey, the selected catalysts are active, selective and productive to yield fuel-like components. Based on this investigation, efficient in-situ atmospheric pyrolysis vapor upgrading with minimum carbon loss and hydrogen consumption can be carried out using a cascade system of proposed catalysts (Fig. 21) in an integrated pyrolysis/upgrading process.

6. Conclusion

This study is targeting to analyze the results of model compound approach research to present the knowledge needed to develop catalysts and processes to upgrade pyrolysis bio-oil. In this investigation, special attentions are drawn on (a) maximizing carbon retention in the upgraded products, (b) minimizing hydrogen consumption in the upgrading processes, and (c) optimizing product fuel properties. The model compounds approach has been utilized to identify the reaction conditions and catalysts that are active and selective for several classes of reactions. Condensation, ketonization and etherization reactions have been investigated to build longer (fuel molecule) carbon chains from small oxygenates (aldehydes, ketones, acids) by using metal oxides and zeolites catalysts. Zeolites and supported metal catalysts could be employed for deoxygenation of furfurals (as models of sugar-derived compounds in bio-oil) and phenolics (lignin derived compound). Alkylation and transalkylation by zeolite and zeolite supported metals improve carbon retention. Based on this profound investigation a set of catalysts have been proposed to be used in a catalytic upgrading cascade process which comprises several consecutive steps for different bio-oil components upgrading. They were selected from four catalyst's classes of zeolites, zeolites supported metals, oxide supported metals and metal oxides. An integrated fast pyrolysis process followed by catalytic bio-oil vapor upgrading reactions has been dedicated to produce high quality and stabilized bio-fuel. The proposed catalytic upgrading process is flexible enough for different reactors configurations. In the future action, authors will intend to comprehensively investigate on in-situ biomass to bio-oil upgrading based on suggested catalysts and process.

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References

[1] Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. Chem Eng J 2003;91:87–102.
[2] Meier D, Faix O. State of the art of applied fast pyrolysis of lignocellulosic materials – a review. Bioresour Technol 1999;68:71–7.
[3] Zhang S, Yan Y, Li T, Ren Z. Upgrading of liquid fuel from the pyrolysis of biomass. Bioresour Technol 2005;96:545–50.
[4] McKendry P. Energy production from biomass (Part 1): overview of biomass. Bioresour Technol 2002;83:37–46.

[5] Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. Renew Sustain Energy Rev 2000;4:1–73.
[6] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 2006;20:848–89.
[7] Ingram L, Mohan D, Bricka M, Steele P, Strobel D, Crocker D, et al. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy Fuels 2007;22:614–25.
[8] Zhang J, Toghiani H, Mohan D, Pittman CU, Toghiani RK. Product analysis and thermodynamic simulations from the pyrolysis of several biomass feedstocks. Energy Fuels 2007;21:2373–85.
[9] Bridgwater AV. Principles and practice of biomass fast pyrolysis processes for liquids. J Anal Appl Pyrolysis 1999;51:3–22.
[10] Elliott DC, Beckman D, Bridgwater AV, Diebold JP, Gevert SB, Solantausta Y. Developments in direct thermochemical liquefaction of biomass: 1983–1990. Energy Fuels 1991;5:399–410.
[11] Lu Q, Li W-Z, Zhu X-F. Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers Manag 2009;50:1376–83.
[12] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004;18:590–8.
[13] Chiaramonti D, Oasmaa A, Solantausta Y. Power generation using fast pyrolysis liquids from biomass. Renew Sustain Energy Rev 2007;11:1056–86.
[14] Pütün E, Ateş F, Pütün AE. Catalytic pyrolysis of biomass in inert and steam atmospheres. Fuel 2008;87:815–24.
[15] Thangalazhy-Gopakumar S, Adhikari S, Gupta RB, Tu M, Taylor S. Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments. Bioresour Technol 2011;102:6742–9.
[16] Zhang H, Xiao R, Wang D, He G, Shao S, Zhang J, et al. Biomass fast pyrolysis in a fluidized bed reactor under N_2, CO_2, CO, CH_4 and H_2 atmospheres. Bioresour Technol 2011;102:4258–64.
[17] Zheng J-L, Wei Q. Improving the quality of fast pyrolysis bio-oil by reduced pressure distillation. Biomass Bioenergy 2011;35:1804–10.
[18] Gayubo AG, Valle B, Aguayo AT, Olazar M, Bilbao J. Pyrolytic lignin removal for the valorization of biomass pyrolysis crude bio-oil by catalytic transformation. J Chem Technol Biotechnol 2010;85:132–44.
[19] Stephanidis S, Nitsos C, Kalogiannis K, Iliopoulou EF, Lappas AA, Triantafyllidis KS. Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: effect of hydrothermal pre-treatment of biomass. Catal Today 2011;167:37–45.
[20] Mercader FdM, Groeneveld MJ, Kersten SRA, Venderbosch RH, Hogendoorn JA. Pyrolysis oil upgrading by high pressure thermal treatment. Fuel 2010;89:2829–37.
[21] Wang Y, He T, Liu K, Wu J, Fang Y. From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. Bioresour Technol 2012;108:280–4.
[22] Oasmaa A, Kuoppala E, Selin J-F, Gust S, Solantausta Y. Fast pyrolysis of forestry residue and pine. 4. Improvement of the product quality by solvent addition. Energy Fuels 2004;18:1578–83.
[23] Junming X, Jianchun J, Yunjuan S, Yanju L. Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics. Biomass Bioenergy 2008;32:1056–61.
[24] Deng L, Fu Y, Guo Q-X. Upgraded acidic components of bio-oil through catalytic ketonic condensation. Energy Fuels 2008;23:564–8.
[25] Adjaye JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: comparative catalyst performance and reaction pathways. Fuel Process Technol 1995;45:185–202.
[26] Adjaye JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: conversion over various catalysts. Fuel Process Technol 1995;45:161–83.
[27] Park HJ, Dong JI, Jeon JK, Yoo KS, Yim JS, Sohn JM, et al. Conversion of the pyrolytic vapor of radiata pine over zeolites. J Ind Eng Chem 2007;13:182–9.
[28] Vitolo S, Bresci B, Seggiani M, Gallo MG. Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading–regenerating cycles. Fuel 2001;80:17–26.
[29] Oasmaa A, Elliott DC, Korhonen J. Acidity of biomass fast pyrolysis bio-oils. Energy Fuels 2010;24:6548–54.
[30] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 2006:106.
[31] Resasco DE. What should we demand from the catalysts responsible for upgrading biomass pyrolysis oil? J Phys Chem Lett 2011;2:2294–5.
[32] Hicks JC. Advances in C–O bond transformations in lignin-derived compounds for biofuels production. J Phys Chem Lett 2011;2:2280–7.
[33] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 2006;106:4044–98.
[34] Béguin P, Aubert J-P. The biological degradation of cellulose. FEMS Microbiol Rev 1994;13:25–58.
[35] Kuhad R, Singh A, Eriksson K-E. Microorganisms and enzymes involved in the degradation of plant fiber cell walls. In: Eriksson KEL, Babel W, Blanch HW, Cooney CL, Enfors SO, Fiechter A, et al., editors. Biotechnology in the Pulp and Paper Industry. Berlin Heidelberg: Springer; 1997. p. 45–125.
[36] Pérez J, Muñoz-Dorado J, de la Rubia T, Martínez J. Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. Int Microbiol: Off J Span Soc Microbiol 2002;5:53–63.
[37] Jørgensen H, Kristensen JB, Felby C. Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities. Biofuels, Bioprod Biorefining 2007;1:119–34.
[38] Nguyen TS, Zabeti M, Lefferts L, Brem G, Seshan K. Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts. Biomass Bioenergy 2013;48:100–10.
[39] Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind Eng Chem Res 2009;48:3713–29.
[40] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol 2005;96:673–86.
[41] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 2002;83:1–11.
[42] Scott DS, Majerski P, Piskorz J, Radlein D. A second look at fast pyrolysis of biomass – the RTI process. J Anal Appl Pyrolysis 1999;51:23–37.
[43] Isahak WNRW, Hisham MWM, Yarmo MA, Yun Hin T-y. A review on bio-oil production from biomass by using pyrolysis method. Renew Sustain Energy Rev 2012;16:5910–23.
[44] Sanchez-Silva L, Lopez-Gonzalez D, Villasenor J, Sanchez P, Valverde JL. Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. Bioresour Technol 2012;109:163–72.
[45] Venderbosch RH, Prins W. Fast pyrolysis technology development. Biofuels, Bioprod Biorefining 2010;4:178–208.
[46] Brown RC, Stevens C. Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power. Hoboken, NJ: Wiley; 2011.
[47] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86:1781–8.
[48] Ball R, McIntosh AC, Brindley J. Feedback processes in cellulose thermal decomposition: implications for fire-retarding strategies and treatments. Combust Theory Model 2004;8:281–91.
[49] Kim T-S, Kim J-Y, Kim K-H, Lee S, Choi D, Choi I-G, et al. The effect of storage duration on bio-oil properties. J Anal Appl Pyrolysis 2012;95:118–25.
[50] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers Manag 2007;48:87–92.
[51] Elliott DC. Historical developments in hydroprocessing bio-oils. Energy Fuels 2007;21:1792–815.
[52] Mullen CA, Boateng AA. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. Energy Fuels 2008;22:2104–9.
[53] Mullen CA, Boateng AA, Hicks KB, Goldberg NM, Moreau RA. Analysis and comparison of bio-oil produced by fast pyrolysis from three barley biomass/byproduct streams. Energy Fuels 2009;24:699–706.
[54] Ausavasukhi A, Sooknoi T, Resasco DE. Catalytic deoxygenation of benzaldehyde over gallium-modified ZSM-5 zeolite. J Catal 2009;268:68–78.
[55] Peralta MA, Sooknoi T, Danuthai T, Resasco DE. Deoxygenation of benzaldehyde over CsNaX zeolites. J Mol Catal A: Chem 2009;312:78–86.
[56] Gaertner CA, Serrano-Ruiz JC, Braden DJ, Dumesic JA. Catalytic coupling of carboxylic acids by ketonization as a processing step in biomass conversion. J Catal 2009;266:71–8.
[57] Gangadharan A, Shen M, Sooknoi T, Resasco DE, Mallinson RG. Condensation reactions of propanal over $Ce_xZr_{1-x}O_2$ mixed oxide catalysts. Appl Catal A: Gen 2010;385:80–91.
[58] Hoang TQ, Zhu X, Lobban LL, Resasco DE, Mallinson RG. Effects of HZSM-5 crystallite size on stability and alkyl-aromatics product distribution from conversion of propanal. Catal Commun 2010;11:977–81.
[59] Pham TT, Crossley SP, Sooknoi T, Lobban LL, Resasco DE, Mallinson RG. Etherification of aldehydes, alcohols and their mixtures on Pd/SiO_2 catalysts. Appl Catal A: Gen 2010;379:135–40.
[60] Do PTM, Crossley S, Santikunaporn M, Resasco DE. Catalytic strategies for improving specific fuel properties. Catal: R Soc Chem 2007:33–64.
[61] Pham TT, Lobban LL, Resasco DE, Mallinson RG. Hydrogenation and hydrodeoxygenation of 2-methyl-2-pentenal on supported metal catalysts. J Catal 2009;266:9–14.
[62] Eom IY, Kim JY, Kim TS, Lee SM, Choi D, Choi IG, et al. Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. Bioresour Technol 2012;104:687–94.
[63] Eom IY, Kim JY, Lee SM, Cho TS, Yeo H, Choi JW. Comparison of pyrolytic products produced from inorganic-rich and demineralized rice straw (*Oryza sativa* L.) by fluidized bed pyrolyzer for future biorefinery approach. Bioresour Technol 2013;128:664–72.
[64] Pham TN, Shi D, Resasco DE. Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase. Appl Catal B: Environ 2014;145:10–23.
[65] Yamada Y, Segawa M, Sato F, Kojima T, Sato S. Catalytic performance of rare earth oxides in ketonization of acetic acid. J Mol Catal A: Chem 2011;346:79–86.
[66] Mentzel UV, Holm MS. Utilization of biomass: conversion of model compounds to hydrocarbons over zeolite H-ZSM-5. Appl Catal A: Gen 2011;396:59–67.
[67] Bjorgen M, Svelle S, Joensen F, Nerlov J, Kolboe S, Bonino F, et al. Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: on the origin of the olefinic species. J Catal 2007;249:195–207.
[68] Ilias S, Bhan A. Tuning the selectivity of methanol-to-hydrocarbons conversion on H-ZSM-5 by co-processing olefin or aromatic compounds. J Catal 2012;290:186–92.
[69] Zakzeski J, Bruijnincx PCA, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev 2010;110:3552–99.
[70] Perego C, Ingallina P. Recent advances in the industrial alkylation of aromatics: new catalysts and new processes. Catal Today 2002;73:3–22.

[71] Zhu X, Mallinson RG, Resasco DE. Role of transalkylation reactions in the conversion of anisole over HZSM-5. Appl Catal A: Gen 2010;379:172–81.
[72] Zhu X, Lobban LL, Mallinson RG, Resasco DE. Bifunctional transalkylation and hydrodeoxygenation of anisole over a Pt/HBeta catalyst. J Catal 2011;281:21–9.
[73] Prasomsri T, To AT, Crossley S, Alvarez WE, Resasco DE. Catalytic conversion of anisole over HY and HZSM-5 zeolites in the presence of different hydrocarbon mixtures. Appl Catal B: Environ 2011;106:204–11.
[74] González-Borja MAn, Resasco DE. Anisole and guaiacol hydrodeoxygenation over monolithic Pt–Sn catalysts. Energy Fuels 2011;25:4155–62.
[75] Sitthisa S, Resasco DE. Hydrodeoxygenation of furfural over supported metal catalysts: a comparative study of Cu, Pd and Ni. Catal Lett 2011;141:784–91.
[76] Bejblová M, Zámostný P, Červený L, Čejka J. Hydrodeoxygenation of benzophenone on Pd catalysts. Appl Catal A: Gen 2005;296:169–75.
[77] Zheng H-Y, Zhu Y-L, Teng B-T, Bai Z-Q, Zhang C-H, Xiang H-W, et al. Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran. J Mol Catal A: Chem 2006;246:18–23.
[78] Srivastava RD, Guha AK. Kinetics and mechanism of deactivation of $PdAl_2O_3$ catalyst in the gaseous phase decarbonylation of furfural. J Catal 1985;91: 254–62.
[79] Sitthisa S, Pham T, Prasomsri T, Sooknoi T, Mallinson RG, Resasco DE. Conversion of furfural and 2-methylpentanal on Pd/SiO_2 and $Pd–Cu/SiO_2$ catalysts. J Catal 2011;280:17–27.
[80] Yu W, Tang Y, Mo L, Chen P, Lou H, Zheng X. Bifunctional Pd/Al-SBA-15 catalyzed one-step hydrogenation–esterification of furfural and acetic acid: a model reaction for catalytic upgrading of bio-oil. Catal Commun 2011;13:35–9.
[81] Yu W, Tang Y, Mo L, Chen P, Lou H, Zheng X. One-step hydrogenation–esterification of furfural and acetic acid over bifunctional Pd catalysts for bio-oil upgrading. Bioresour Technol 2011;102:8241–6.
[82] Graça Is, Comparot J-D, Sb Laforge, Magnoux P, Lopes JM, Ribeiro MF, et al. Influence of phenol addition on the H-ZSM-5 zeolite catalytic properties during methylcyclohexane transformation. Energy Fuels 2009;23:4224–30.
[83] Graça I, Comparot JD, Laforge S, Magnoux P, Lopes JM, Ribeiro MF, et al. Effect of phenol addition on the performances of H–Y zeolite during methylcyclohexane transformation. Appl Catal A: Gen 2009;353:123–9.
[84] Popov A, Kondratieva E, Goupil JM, Mariey L, Bazin P, Gilson J-P, et al. Bio-oils hydrodeoxygenation: adsorption of phenolic molecules on oxidic catalyst supports. J Phys Chem C 2010;114:15661–70.
[85] Graça I, Lopes JM, Ribeiro MF, Badawi M, Laforge S, Magnoux P, et al. n-Heptane cracking over mixtures of HY and HZSM-5 zeolites: influence of the presence of phenol. Fuel 2012;94:571–7.
[86] Gayubo AG, Aguayo AT, Atutxa A, Aguado R, Olazar M, Bilbao J. Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. II. Aldehydes, ketones, and acids. Ind Eng Chem Res 2004;43:2619–26.
[87] Gayubo AG, Aguayo AT, Atutxa A, Aguado R, Bilbao J. Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. I. alcohols and phenols. Ind Eng Chem Res 2004;43:2610–8.
[88] Meng X, Xu C, Gao J. Coking behavior and catalyst deactivation for catalytic pyrolysis of heavy oil. Fuel 2007;86:1720–6.
[89] Bibby DM, Howe RF, McLellan GD. Coke formation in high-silica zeolites. Appl Catal A: Gen 1992;93:1–34.
[90] Srivastava R, Choi M, Ryoo R. Mesoporous materials with zeolite framework: remarkable effect of the hierarchical structure for retardation of catalyst deactivation. Chem Commun 2006;43:4489–91.
[91] Kim J, Choi M, Ryoo R. Effect of mesoporosity against the deactivation of MFI zeolite catalyst during the methanol-to-hydrocarbon conversion process. J Catal 2010;269:219–28.
[92] Jae J, Tompsett GA, Lin Y-C, Carlson TR, Shen J, Zhang T, et al. Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis. Energy Environ Sci 2010;3: 358–365.
[93] Roberts VM, Stein V, Reiner T, Lemonidou A, Li X, Lercher JA. Towards quantitative catalytic lignin depolymerization. Chem – Eur J 2011;17:5939–48.